

THE ANALYSIS OF VEGETATION
BY X-RAY FLUORESCENCE
SPECTROMETRY
PART 1: CHLORINE, SULPHUR
PHOSPHORUS, CALCIUM
POTASSIUM, SILICON

November 1980



Ministry
of the
Environment

The Honourable
Harry C. Parrott, D.D.S.,
Minister

Graham W. S. Scott, Q.C.,
Deputy Minister

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BY X-RAY FLUORESCENCE SPECTROMETRY
PART 1: CHLORINE, SULPHUR, PHOSPHORUS
CALCIUM, POTASSIUM, SILICON

by

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Laboratory Services Branch
Ontario Ministry of the Environment

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INTRODUCTION

Of the many techniques available for monitoring the degree of air pollution in any given area, the examination of vegetation for air pollution damage is a convenient and effective technique. Throughout the Province of Ontario, surveys are carried out by the Regions and the Air Resources Branch (Phototoxicology Section) of the Ministry of the Environment to assess vegetation damage caused by air pollutants. Vegetation is examined by Field experts for visible damage and chemically analysed for a wide range of potentially toxic elements. The current method of analysis for metals is by Atomic Absorption Spectroscopy (AAS).

With the acquisition of an X-ray spectrometer by the Laboratory Services Branch, an extensive comparison was completed of several methods, including XRF, for the analysis of sulphur, chlorine and phosphorus¹. As a result, the XRF method was adopted for the analysis of sulphur and several thousand samples have been analysed for this element to date. Later on, feasibility studies were conducted on the determination of other elements such as aluminum, silicon and titanium.

In 1979, a new project was initiated to investigate the analysis of trace metals (report in preparation), as well as to re-evaluate the previous method for sulphur, chlorine and phosphorus, taking into consideration the matrix effects caused by the other major elements. These studies have been facilitated by the automation of the X-ray spectrometer by means of a "logic controller" which can be controlled by computer of teletype.

This report represents the progress achieved to date on the analysis of S, Cl, P, Ca, K, Si, six elements which constitute the major portion of the "matrix elements" in plant material.

EXPERIMENTAL

XRF PROCEDURE

Pellets prepared for the 1973 project were used for the present re-investigation of Cl, S and P. The reader is referred to reference (1) for the method of preparation of these samples. No degradation of these pellets was observed over the six year storage period.

Pellets for the determination of Si, Ca, and K were prepared by mixing 2.00 g of dried vegetation with 0.50 g of Hoechst "C" wax (used as a binder). The mixture was vigorously mixed in a plastic vial and the mixture pelletized at 25 tons for 30 seconds. A polished die 40 mm in diameter was used to shape the pellets.

All measurements were performed using a Siemens SRS X-ray spectrometer. Instrument parameters used in the analysis are shown in Appendix 1. The operation of the instrument is totally automated with instructions sent to the SRS spectrometer by the "logic controller" via a teletype. The output information (counting time and total counts) is recorded on paper tape. This data set is subsequently stored on cassette tape and evaluated by a Hewlett Packard 9825 calculator.

CHEMICAL PROCEDURES

S, Cl and P were determined using AOAC procedures¹. The Si concentration of 40 vegetation samples was determined by fusion of an ashed vegetation sample with KOH, a method based on the determination of Si in rock samples⁵. A 1.00 g sample of vegetation was reduced to ash in a nickel crucible by heating the sample for three hours at 550°C in a muffle furnace. The sample was then fused with 1 g of KOH, the melt dissolved in distilled water and acidified with HCl to a pH of 6.5. The sample was quantitatively transferred to a 25 ml volumetric flask and diluted to the mark. A silicon standard stock solution was prepared by the same method using high purity SiO₂. Working standard solutions for AAS were prepared from the stock solution and from a solution containing CaCO₃, KCl and

MgCo₃ dissolved in HCl, (a synthetic matrix representative of real samples).

The Ca and K levels in 80 vegetation samples were determined by atomic absorption and atomic emission spectroscopy respectively. For this method, a sample of 0.20 g of dried vegetation was digested with a mixture of 4 ml of nitric and 1 ml perchloric acids, in a 10 ml graduated test tube and refluxed for 24 hours. At the end of this period, the solution was diluted to 10 ml with distilled water. Samples requiring a Ca determination were diluted either 10-fold or 100-fold with a 1% La(NO₃)₃ solution and analyzed by AAS. Samples requiring a K determination were diluted 100-fold with distilled water and analyzed by atomic emission spectroscopy. A Varian AA5 Atomic Absorption Spectrophotometer was used for both determinations.

NBS certified materials were used as control standards.

XRF ARTIFICIAL STANDARDS

Standards were prepared by adding solutions of known concentrations of the desired elements to 3.00 g of microcrystalline cellulose in a 100 ml beaker. Distilled water was added to just submerge the cellulose in the solution. The mixture was stirred well and dried at 60°C in an oven. When dry, the cellulose was ground in an agate mortar. Two grams of the sample were mixed with 0.5 g of wax and pelletized in the same way as the vegetation samples.

DISCUSSION

MATRIX CORRECTION

a) Theory:

The method used here to correct for matrix effects is that developed by K. Norrish and J.T. Hutton² in 1977. The reader is referred to their paper for a complete description of the procedure.

Briefly, it is assumed that the equation

$$C_i = S (R_p - R_b) u_i \quad (1)$$

is applicable to the vegetation samples. C_i is the concentration of element i , R_p is the peak fluorescent intensity, R_b is the background intensity and u_i is the mass absorption coefficient of the sample when measured at the analytical line of element i . The value of u_i is directly dependent on the matrix composition of the sample. S is a constant dependent on the instrument used for the analysis.

If it is assumed that R_b is zero, as is generally the case, then

$$C_i \propto R_p u_i \quad (2)$$

or

$$C_i/u_i \propto R_p \quad (3)$$

or

$$C_i^* \propto R_p \quad (4)$$

where C_i^* is the "nominal" concentration of element i and is equal to C_i/u_i . Clearly, a plot of C_i^* vs R_p will yield a straight line.

The mass absorption coefficient of the vegetation samples is not measured directly; instead a value is calculated. In order to perform this calculation, it is assumed that the vegetation sample consists of pure cellulose, to which has been added a small percentage (0.02-5%) of the matrix elements. The value of u_i is obtained from the relationship

$$u_i = u_{i0} + \sum_{k=1}^6 u^*_{ik} C_k$$

where u_i is, as before, the mass absorption coefficient of the sample at the wavelength of the $K\alpha$ line of i and u^*_{ik} is the mass absorption coefficient of the element k measured at the wavelength of the $K\alpha$ line of i . The values for u^*_{ik} are obtained from Appendix 1 of ref. 3). C_k is the concentration of element k and u_{i0} is the mass absorption coefficient of pure cellulose (calculated from Table I of ref. (3)). A matrix adjusted or as it is termed here, a matrix corrected calibration curve is then prepared by plotting C_i^* vs R_p . Matrix corrections are more severe for the heavier elements (Ca, K) while the lighter elements (Si, P, S) require little or no correction.

b) Calibration Procedure

In order to prepare a matrix corrected calibration curve for an element, for example K, a knowledge of not only the K concentration, but also a knowledge of

the concentrations of all other matrix elements is required. In their original analysis, Norrish and Hutton had 12 vegetation samples whose matrix composition had been analyzed thoroughly by five independent investigators.

Since the laboratory had 190 Cl, P, S and Si analysed samples in storage, it required that only 80 additional samples be analyzed for K or Ca by atomic emission spectroscopy or AAS respectively. Although this set now contained samples analyzed for all six elements, in general, the concentration of only one element was known for any one particular sample. To supplement this set artificial standards were prepared by doping cellulose with known amounts of the matrix elements. By using these artificial standards, a "zeroth order" approximation to the matrix corrected calibration curve for each element was prepared by the methods outlined above. The curves were generally of poor quality and give a particularly poor estimate for the Cl level in the vegetation samples. A reiterative process was used to prepare the final calibration curves. The procedure is as follows:

A matrix corrected calibration curve for Si was prepared using the vegetation samples whose Si concentrations had previously been determined by AAS. The concentrations of the other matrix elements that were required in the calculations were estimated from the artificial standard curves. Si was chosen since

it is least affected by matrix effects; that is, it has the lowest atomic number of the six elements studied. Any large error in the Ca, K, Cl, S and P levels resulted in only small errors in the calibration procedure. Thus a good "first order" approximation to the Si calibration curve was obtained. Next, a matrix corrected curve for P (the element having the next highest atomic number) was evaluated using the "zeroth order" curves of Ca, K, Cl and S and "first order" curve of Si. This procedure was followed until "first order" calibration curves existed for all elements. This represented the end of the first cycle. The process was repeated again for Si using the previously determined "first order" curves of the other matrix elements. Each element was then done in turn as before. Three cycles were required for convergence. The results for the individual elements are presented below.

Silicon: Table 1 is a collection of the data obtained for Si while Figures 1 (a) and (b) show a plot of the fluorescent intensity vs matrix and non-matrix corrected Si concentration respectively. The results for the artificial standards (solid squares) is presented for comparison. Table 1 also gives the standard deviation (σ), precision (95%), lower detection limit (95%) and accuracy of the analysis. These quantities are defined in reference (4). The values quoted in Table 1 were

calculated from the data obtained from 10 determinations of NBS orchard leaves. Since the value of σ was not evaluated using data close to zero, the detection limit of 0.03% is probably high.

The samples are clearly partitioned into two groups: those with Si <0.5% and those with Si >1.0%. These represent foliage and grass samples respectively. The large scatter of the grass samples may be attributed to insufficient or non-uniform grinding of these samples. Unfortunately, no NBS certified material could be included in this set since no values for Si were reported. Clearly, in the case of silicon, matrix correction has no discernable effect on the quality of the fit for the samples considered in this study.

Phosphorus, Sulphur, Chlorine: The classical methods used to determine the concentrations of these elements were described in detail in the 1973 report. The results of the present XRF analysis are presented in Tables 2, 3 and 4. A comparison of the matrix corrected and non-matrix corrected curves is presented in Figures 2-4, (a) and (b). Matrix correction is not necessary for the element S and P while a modest improvement is shown for the Cl determination.

The full squares of figures 2(a) and (b) represent the values obtained for four of the NBS materials. All points except that for tomato leaves lie below the calibration line produced from the phosphorous AOAC

analysed vegetation samples. NBS material is more finely ground than the routine vegetation samples and thus may behave differently in the X-ray beam. In no case is the discrepancy between the certified and XRF phosphorous levels greater than 12%.

The full squares of figure 3 (a) and (b) represent the counts obtained for S from the artificial standards. As was generally the case, only the data obtained from the three or four artificial standards with concentration of Si, P and S less than or equal to 1%, fell near the calibration line. The counts from the other pellets were considerably less than those predicted by the calibration line, inspite of the correction. The Si levels in these pellets were quite high (3-4%) and appear to have had a greater attenuating effect than that predicted by theory. These levels are considerably higher than those found in vegetation samples. The only certified S concentration reported for the NBS materials is for orchard leaves. The agreement between it (0.190%) and the XRF value (0.191%) is excellent.

A quadratic equation of the form $y = a_0 + a_1x^2$ was used to fit the vegetation data for Cl, in addition to the usual linear fit. These curves are depicted in figures 4(a) to 4(c). Inspection of Table 5(a) shows that the quadratic curve fits the data better than the linear curve in the range 0 to 0.1% Cl. The data for this Table was generated from the dilution of NBS orchard leaves with Heochst "C" wax. In the range from

0.1% to 1% the linear and quadratic curve fit the data equally well, as verified by the dilution of NBS spinach (Table 4(b) and from the data for the Inter-lab Comparison (Table 5(c)).

Three methods were used to obtain the data for the latter Table. The first was obtained from the routine Automated Colourimetric Method (AC) in which the vegetation sample is combusted in a muffle furnace and analysed colourimetrically. The routine procedure has been optimized for F^- analyses and losses of Cl^- are known to occur. The second method involves combustion of the vegetation sample in a Schoniger Flask followed by a colourimetric analyses (SFAC). The third is the XRF analysis based on a calibration curve obtained from the AOAC analysed samples.

An obvious bias exists between the XRF or SFAC data and the AC data. The AC method appears to under-recover by about 30%. Inspection of figures 5(a) and 5(b) shows that the quadratic XRF calibration curve will allow the inclusion of the two high Cl samples. If these points are included in the linear XRF plot (figure 5(b)) their weight severely distorts the "best" straight line.

Recovery tests were undertaken by spiking NBS orchard leaf samples with varying amounts of KCl. The recoveries are generally good with the XRF quadratic curve over-recovering by 8%, on average. This may

indicate that the AOAC Cl analysis, on which the X-Ray calibration depends, is in error. Additional data will be obtained when the XRF Cl method goes "on-line" and further SFAC data become available. The Routine XRF Cl method calls for 1 in 20 samples to be reanalysed by SFAC in addition to those samples whose Cl level is greater than 1.5%.

The standard deviations, precisions and detection limites stated in Tables 2 to 4 were determined from the data obtained from NBS orchard leaves. As the P and S concentration in these two materials are well removed from zero, the detection limit is somewhat high.

Calcium, Potassium: Tables 6 and 7 contain the data for Ca and K respectively. The standard deviations quoted in this Table were determined for NBS orchard leaves and represent a standard deviation for the middle range. The matrix corrected calibration curves for these two elements are given in figures 6(a) and 7(a). The solid circles are the results obtained for the NBS certified material. Matrix correction for K and Ca in the vegetation samples is significant. In the case of K, all points for the NBS certified material lie above the calibration line, similar to the effect observed in the determination of phosphorous. In the case of Ca, the certified materials are scattered about the calibration line.

Table 6(b) shows the per cent recovery of K for the KCl spiked orchard leaves (see also page 12). Except at the very low end, the recovery for K is satisfactory. It is interesting to note that the addition of 44 mg of K has reduced the fluorescent intensity of Ca in the sample by 26%. The determined Ca concentration remained constant to within 3% because of the matrix correction procedure.

A plot of the matrix effect for the NBS materials is presented in figures 8 and 9. The matrix correction procedure for K is significant in that it reduces the scatter of the points about the calibration line. The correction for Ca in the NBS material is somewhat less striking although some improvement is observed. It appears that the very high level of K in the tomato leaves (4.5%) causes an overcorrection of the data. An undercorrection is observed in the determination of Ca in NBS spinach leaves.

The calibration curves described above are used to calculate the "nominal" concentration (C_i^*) of the matrix elements in the vegetation samples.

Since

$$C_i = C_i^* \cdot u_i$$

$$\text{then } C_i = C_i^* \cdot (u_{i0} + \sum_{k=1}^6 u_{ik}^* C_k) \quad i = 1 \text{ to } 6$$

$$k = 1$$

Since values for C_k (the "true" concentration) are, at present, unknown, then C_k on the right hand side of

equation (4) is replaced by C_k^* and a value for C_i is then calculated. This procedure is followed for all six elements and results in a "first order" approximation to the true value of C_i ($i = 1$ to 6). The procedure is repeated using the "first order" values for C_k and continues until convergence is reached.

A summary of the standard deviation, precision detection limit and accuracy for all six elements is presented in appendix 2.

CONCLUSIONS

XRF spectroscopy has been shown to be a reliable, accurate and rapid method for the determination of the matrix elements in vegetation. Matrix corrected calibration curves have been obtained for Ca, K, Cl, P, S and Si. It has been shown that matrix correction is necessary for the determination of Ca and K and that an improvement is obtained for the determination of Cl. The matrix correction procedure was not necessary for the element S, P and Si. However, as a safeguard against highly contaminated samples, the matrix correction procedure should still be used for these elements.

REFERENCES

- (1) J. A. Pimenta, "Vegetation Analyses by X-Ray Fluorescence. Part 1: Sulphur, Chlorine, Phosphorous". Ontario Ministry of the Environment, 1973.
- (2) K. Norrish and J. T. Hutton, X-Ray Spectr. 6(1), 6-11 (1977).
- (3) K. F. J. Heinrich, in "The Electron Microprobe" edited by T. D. McKinley, K. F. J. Heinrich and D. B. Wittry, p 296. John Wiley and Sons, Inc., New York (1966).
- (4) D. E. King, "Quality Control and Data Evaluation Procedures". Ontario Ministry of the Environment, 1976.
- (5) Dvleřal, Povendra and řulcek, "Decomposition Techniques in Inorganic Analyses", London Cliffe Books Ltd., London p 103.

APPENDIX I

INSTRUMENTAL PARAMETERS OF THE XRF SPECTROMETER

Element	Angle(^o)	Detector	Pulse Height Analyzer Setting (v)	Collimation	Counting Period (sec)	Crystal	Order
Ca	100.27	F/C	1.5	.4	4	PET	2
K	117.54	F/C	1.5	.4	4	PET	2
P	133.27	F/C	1.5	.4	4	Graphite	1
Cl	65.49	F/C	1.5	.4	4	PET	1
S	106.42	F/C	1.5	.4	4	Graphite	1
Si	109.21	F/C	1.5	.4	4	PET	1

F/C Flow Proportional Counter

Power 45 KV, 30 mA

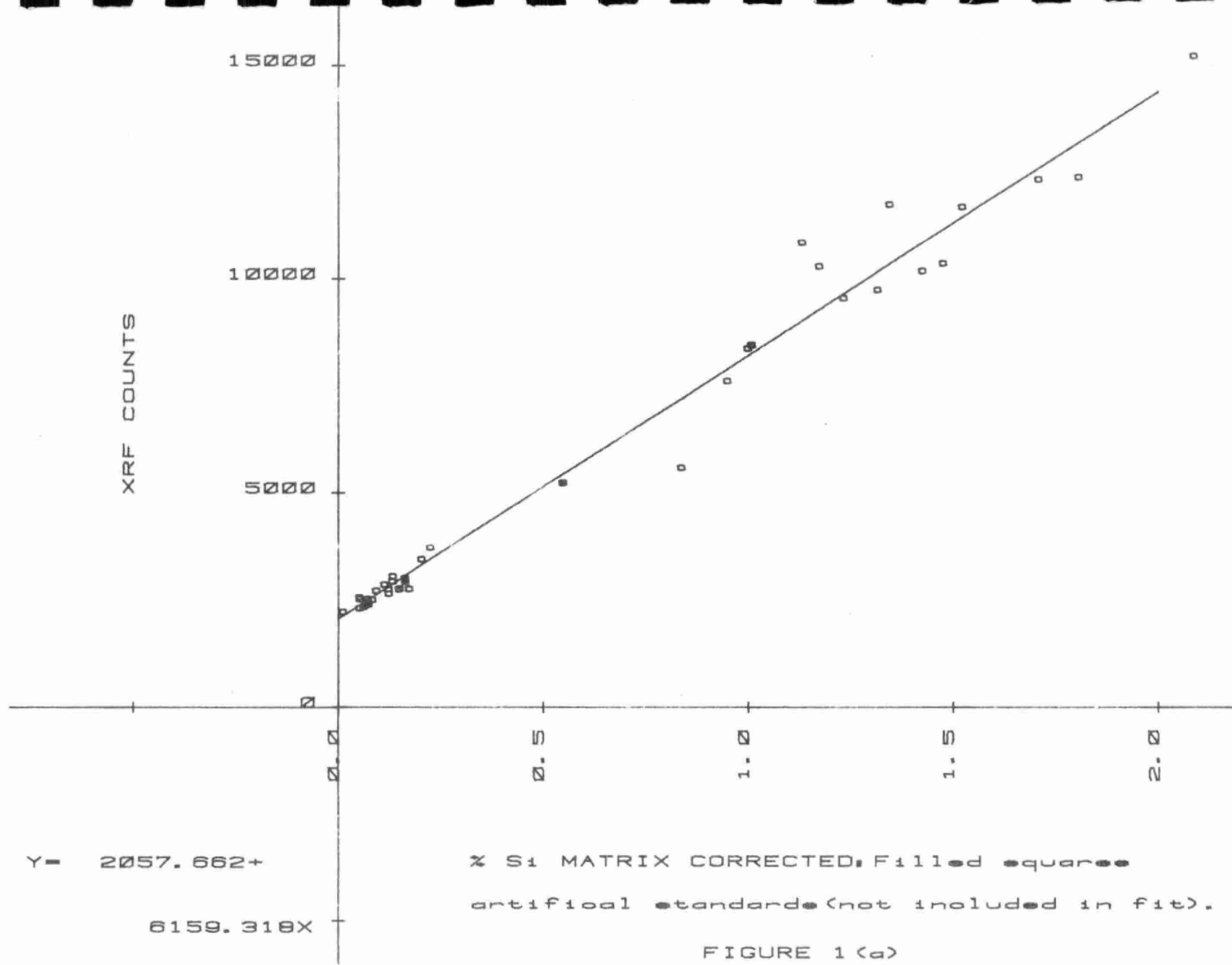
PET Pentaerythritol Crystal

N.B. Angles were peaked for maximum intensity using corresponding elemental standards.

APPENDIX 2

RANGE, ACCURACY, PRECISION, DETECTION LIMITS FOR THE 6 MATRIX ELEMENTS IN VEGETATION

Element	Range	Accuracy	Precision	Lower Detection Limit
Silicon	0 - .5%	± 0.02%	0.03%	0.03%
	1.0 - 2.0%	± 0.10%		
Phosphorus	0 - 0.2%	± 0.01%	0.02%	0.02%
	0.2 - 0.4%	± 0.02%		
	0.4 - 0.6%	± 0.03%		
Sulphur	0 - 0.5%	± 0.025%	0.02%	0.02%
	0.5 - 1.0%	± 0.035%		
	1.0 - 2.0%	± 0.040%		
	2.0 - 4.0%	± 0.50%		
Chlorine	0 - 0.5%	± .02%	0.01%	0.01%
	0.5 - 1.0%	± .03%		
	1.0 - 3.0%	± .10%		
Potassium	0 - 1.0%	± 0.10%	0.04%	0.02%
	1.0 - 2.0%	± 0.07%		
	2.0 - 4.0%	± 0.12%		
Calcium	0 - 1.0%	± .06%	0.07%	0.02%
	1.0 - 2.5%	± .10%		
	2.5 - 4.5%	± .19%		



$$Y = 2057.662 +$$

$$6159.318X$$

$$R = 0.990$$

% Si MATRIX CORRECTED: Filled squares
artificial standards (not included in fit).

FIGURE 1(a)

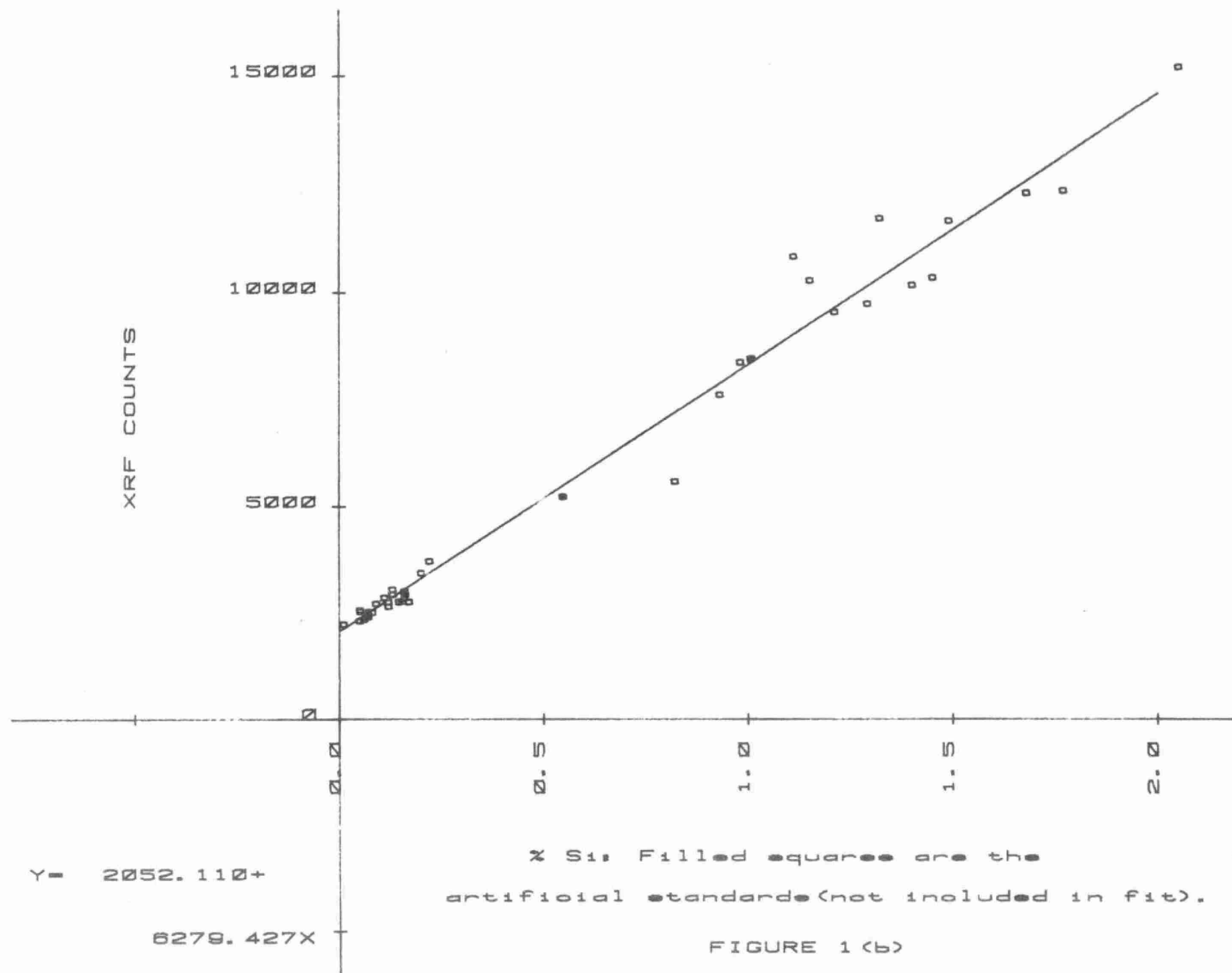


TABLE 1
SILICON AAS vs XRF

		%Si	%Si	%			%Si	%Si	%			%Si	%Si	%
Sample	Type	AAS	XRF	Diff	Sample	Type	AAS	XRF	Diff	Sample	Type	AAS	XRF	Diff
316W	grass	1.40	1.26	10	342W	Manitoba Maple	0.12	.10	16	NBS	orchard leaves	0.15	0.16	-6
316NW	grass	1.45	1.33	8	342NW	Manitoba Maple	0.12	.09	20	NBS	tomato leaves	-	.71	
318W	Manitoba Maple	0.07	0.06	13	343W	grass	1.29	1.23	5	NBS	pine needles	-	.11	
319NW	grass	1.77	1.65	7	343NW	grass	1.49	1.54	3	NBS	spinach leaves	-	.18	
324NW	Manitoba Maple	0.13	0.16	-22	345NW	Manitoba Maple	0.08	0.07	8	NBS	wheat flour	-	.02	
327W	Manitoba Maple	0.16	0.15	6	346W	grass	1.11	1.40	-20					
328W	grass	1.68	1.65	2	346NW	grass	1.32	1.55	-17					
328NW	grass	2.05	2.11	-2	348W	Manitoba Maple	0.07	0.05	25					
330W	Manitoba Maple	0.20	0.22	-10	349W	grass	0.82	0.57	31					
333NW	Manitoba Maple	0.11	0.12	-3	413W	plum	0.06	0.03	44	$\sigma = 0.01$ precision: 0.03% det. limit: 0.03% accuracy: (0-0.5%): $\pm 0.02\%$ (1.0-2.0%): $\pm 0.10\%$				
336W	Manitoba Maple	0.05	0.08	-60	413NW	plum	0.17	0.11	34					
336NW	Manitoba Maple	0.05	0.07	-40	423W	plum	0.07	0.06	20					
337W	grass	0.93	0.89	-4	423NW	plum	0.16	0.14	13					
337W	grass	0.98	1.01	3	432W	apple	0.05	0.04	18					
339W	Manitoba Maple	0.07	.07	18	432NW	apple	0.15	0.14	13					
339NW	Manitoba Maple	0.09	0.11	13	438W	sour cherry	0.01	0.02	-100					
340W	grass	1.15	1.32	1	438NW	sour cherry	0.13	0.14	-12					
340NW	grass	1.21	1.20		444NW	plum	0.22	0.26	-17					

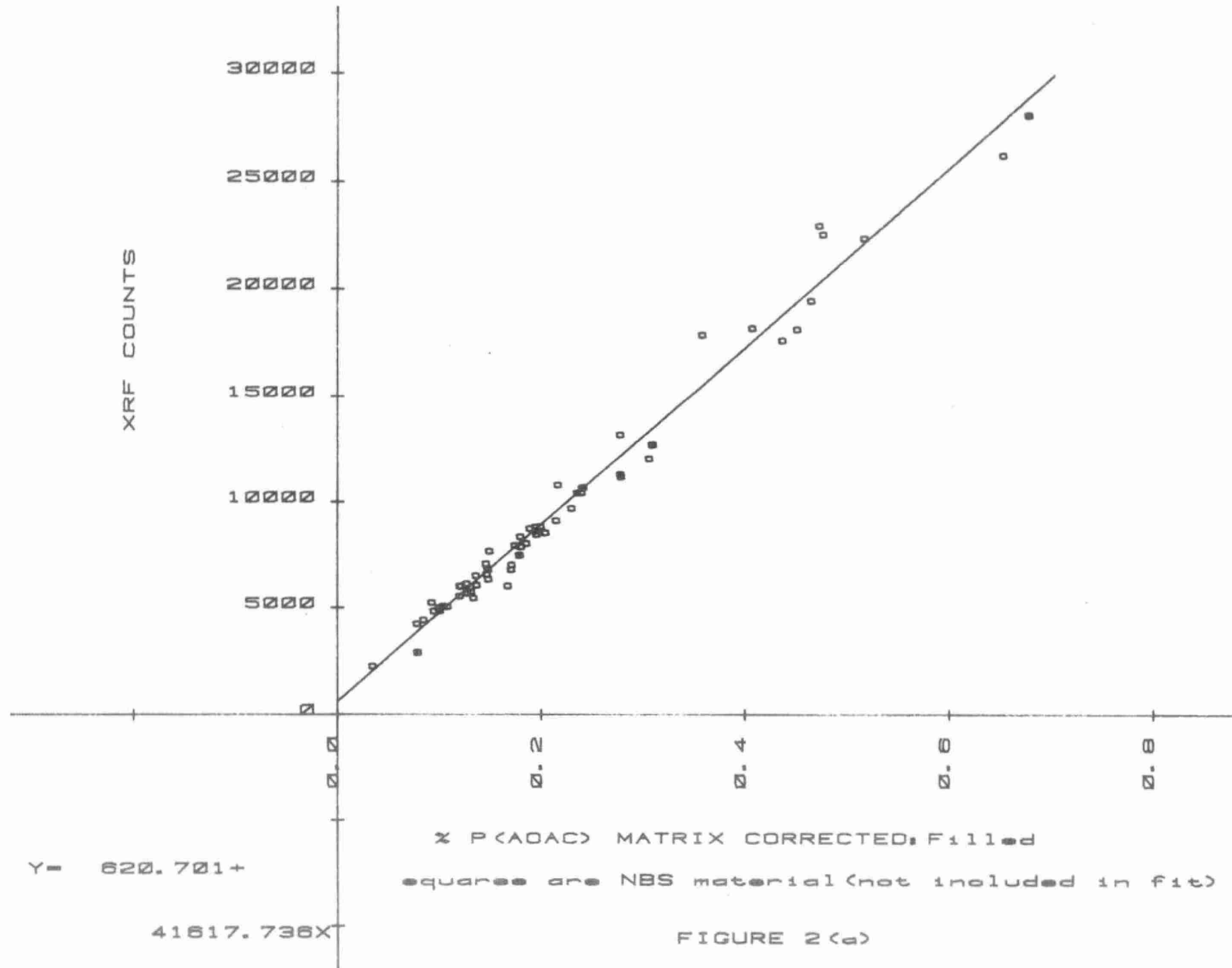
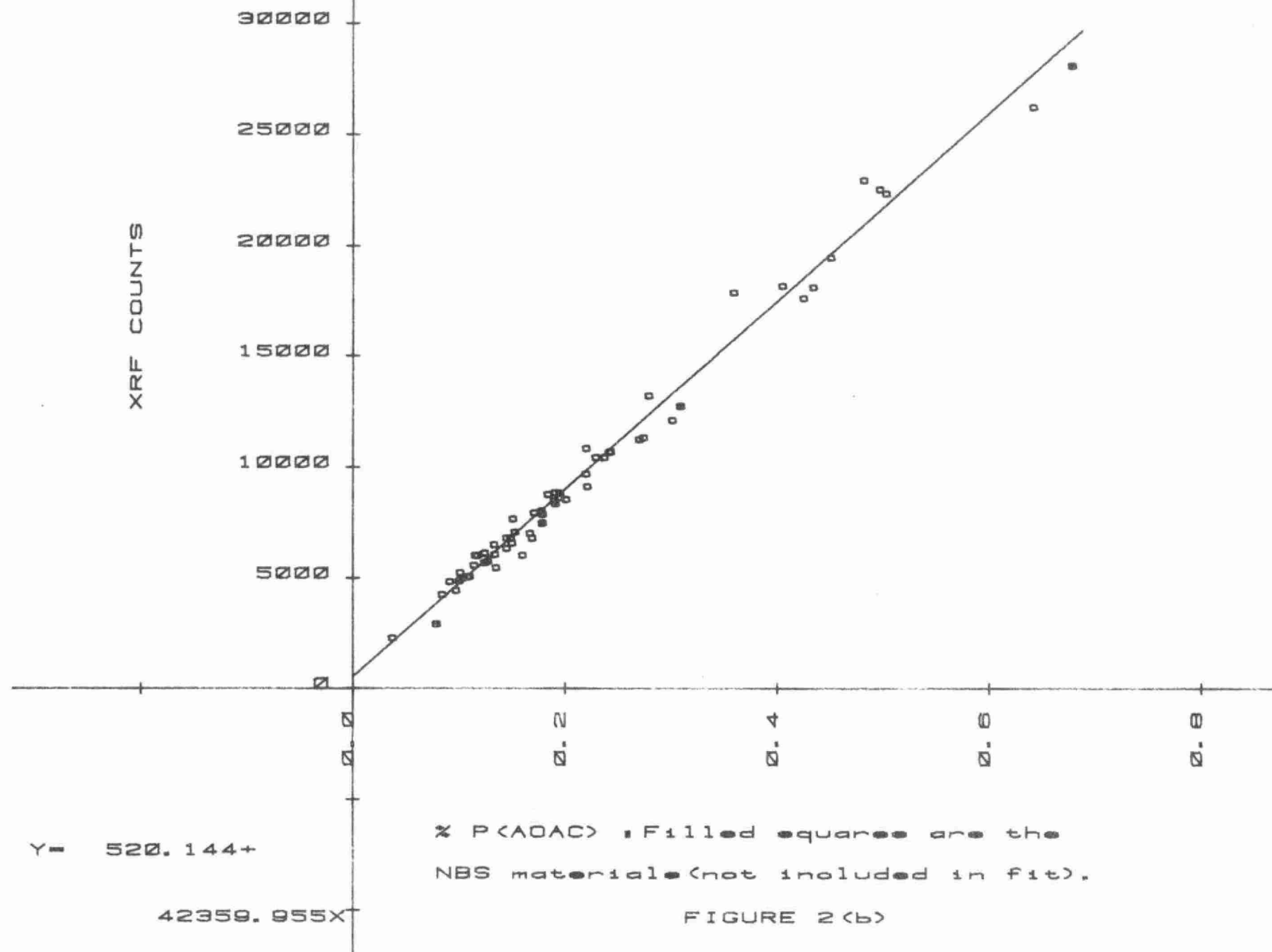


FIGURE 2(a)



% P(AOAC) : Filled squares are the
NBS materials (not included in fit).

FIGURE 2(b)

$R = 0.992$

TABLE 2
PHOSPHORUS , AOAC VS XRF

Sample	Type	%P	%P	%	Sample	Type	%P	%P	%	Sample	Type	%P	%P	%
		AOAC	XRF	Diff			AOAC	XRF	Diff			AOAC	XRF	Diff
5513W	coniferous	0.114	0.114	0	433W	deciduous	0.503	0.510	-2	1681NW	forage	0.144	0.147	-5
5132W	coniferous	0.115	0.125	-9	437NW	deciduous	0.301	0.272	10	6142NW	forage	0.195	0.199	-2
5148W	coniferous	0.160	0.125	21	1680NW	dogwood	0.171	0.173	-1	5671NW	forage	0.152	0.172	-13
3001NW	coniferous	0.127	0.120	6	3385NW	dogwood	0.201	0.188	6	3094W	forage	0.084	0.095	-13
3089W	coniferous	0.117	0.126	8	2351NW	dogwood	0.167	0.151	10	1892NW	forage	0.102	0.108	-6
5518W	coniferous	0.091	0.098	8	3003NW	dogwood	0.229	0.230	-1	5537NW	forage	0.153	0.164	-7
1438NW	coniferous	0.191	0.190	1	4181W	ragweed	0.482	0.549	-14	3330NW	oats	0.037	0.043	-16
5126NW	deciduous	0.451	0.441	2	382NW	ragweed	0.135	0.118	12	4198NW	grass	0.191	0.199	-4
5515W	deciduous	0.178	0.172	3	2357NW	ragweed	0.279	0.305	-10	2589NW	grass	0.220	0.251	-14
6502W	deciduous	0.220	0.209	5	1885NW	tansy	0.274	0.254	7	2596NW	grass	0.243	0.244	-1
6146W	deciduous	0.184	0.191	-4	4427W	gladiolus	0.101	0.122	-20	3013NW	grass	0.110	0.115	-4
5516W	deciduous	0.145	0.146	-1	4451NW	gladiolus	0.100	0.102	-2	356NW	grass	0.497	0.552	-11
6503NW	deciduous	0.434	0.406	6	4350NW	gladiolus	0.124	0.130	-5	3326NW	corn	0.221	0.212	4
3413W	deciduous	0.133	0.139	7	4293NW	gladiolus	0.179	0.174	3	1682W	corn	0.097	0.106	-9
2667NW	deciduous	0.145	0.135	7	5127W	fern	0.242	0.244	-1	1683NW	soy	0.108	0.107	-1
4187W	deciduous	0.237	0.234	1	2605NW	thorn	0.134	0.129	4	1726W	tomato	0.150	0.147	2
435NW	deciduous	0.405	0.421	4	4132NW	honeysuckle	0.149	0.149	-2	5163NW	tomato	0.425	0.399	6
353NW	deciduous	0.642	0.606	5	2355W	thorn	0.124	0.118	5	3533W	rhubarb	0.270	0.248	8
3008NW	deciduous	0.190	0.184	3	1890NW	cherry	0.169	0.148	12	816W	potato	0.359	0.418	-6
										NBS	orchard leaves	0.21	0.211	-1
											cert value			
										NBS	tomato leaves	0.34	0.330	13
										NBS	pine needles	0.12	0.135	-12
										NBS	spinach leaves	0.55	0.585	-6
										NBS	wheat flour	-	0.144	-

$\sigma = 0.005$
precision : 0.015%
det. limit: 0.016%
accuracy :
(0-0.2%): $\pm .010$
(0.2-0.4%): ± 0.020
(0.4-0.6%): ± 0.030

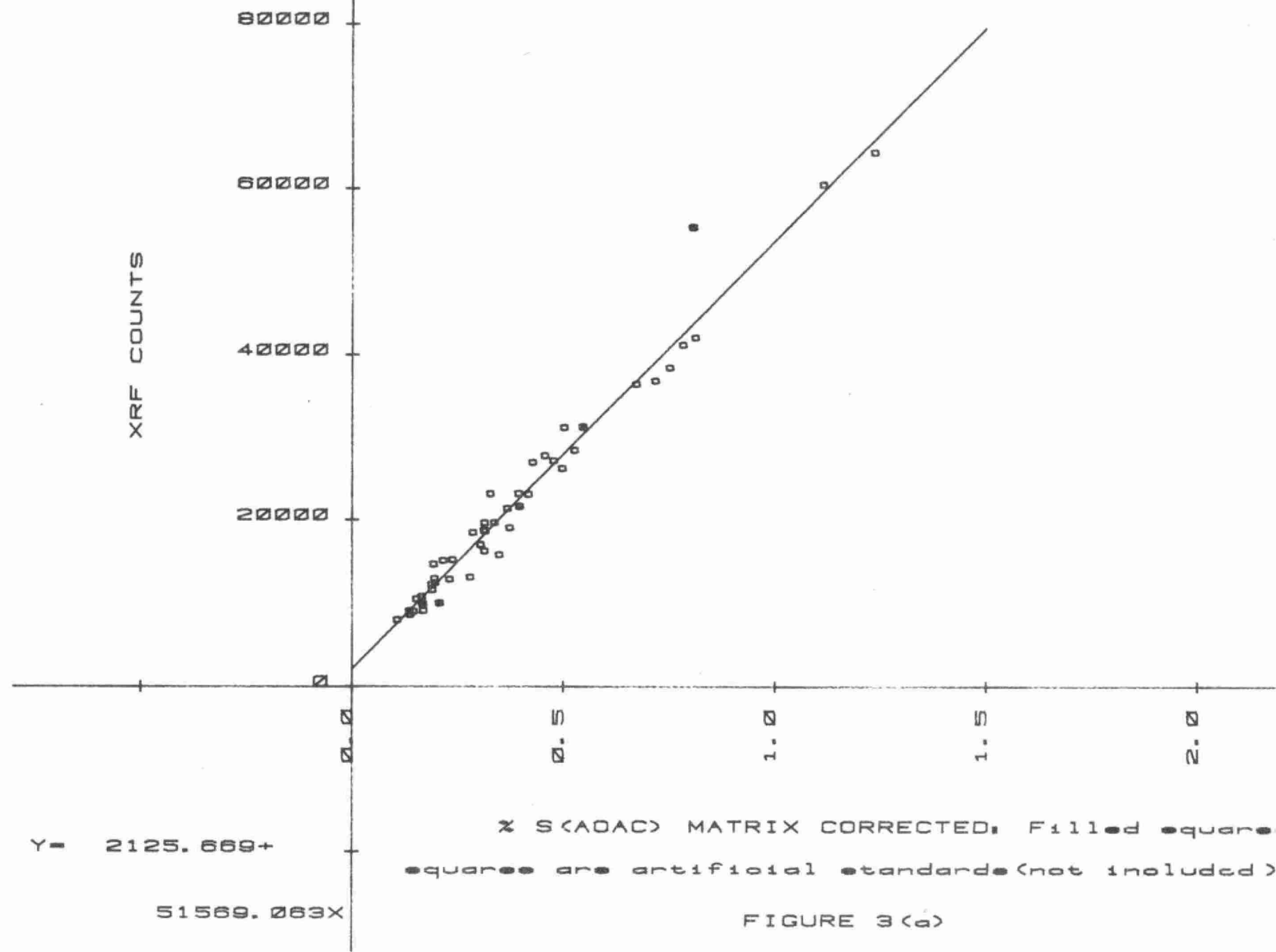


FIGURE 3(a)

R = 0.994

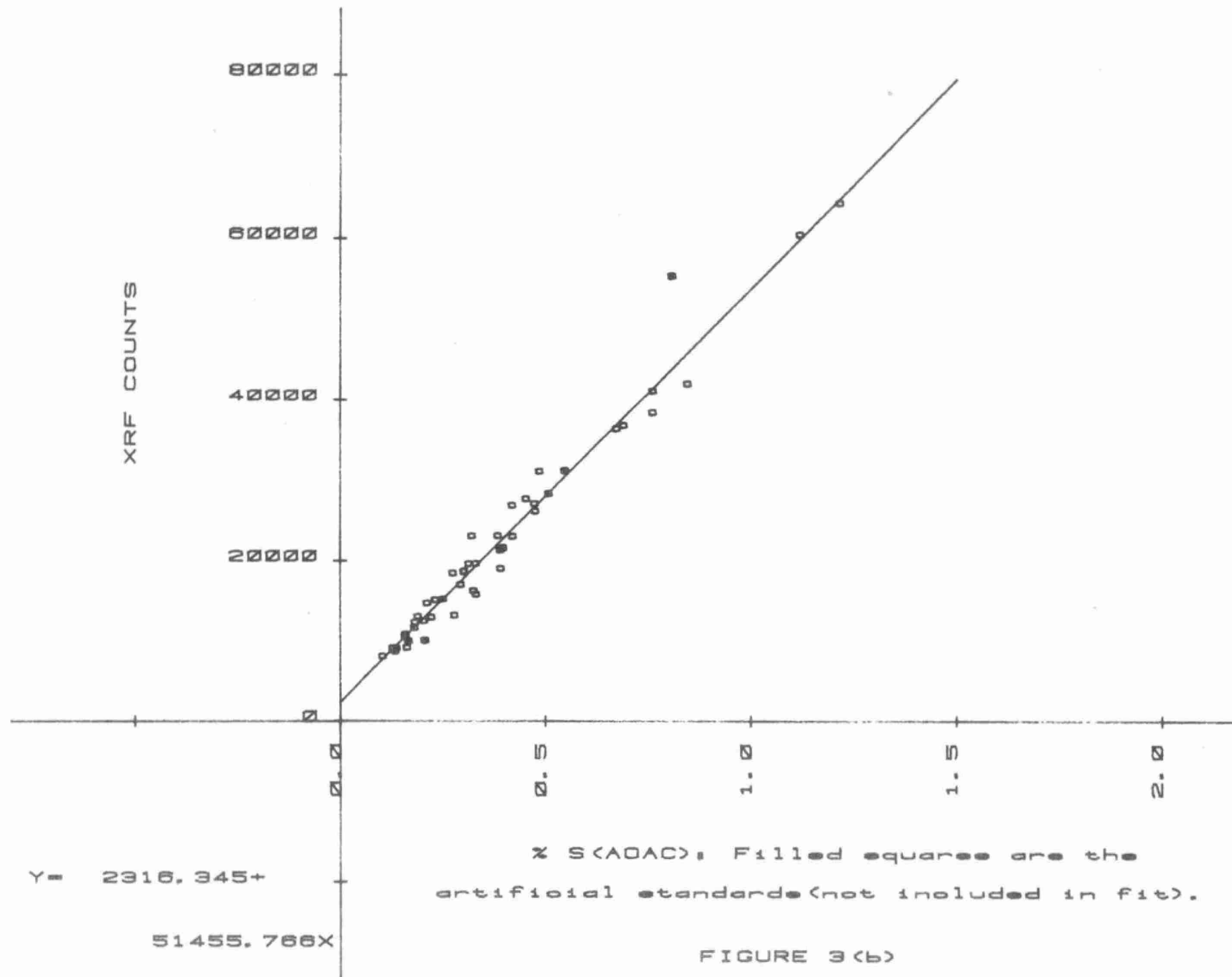
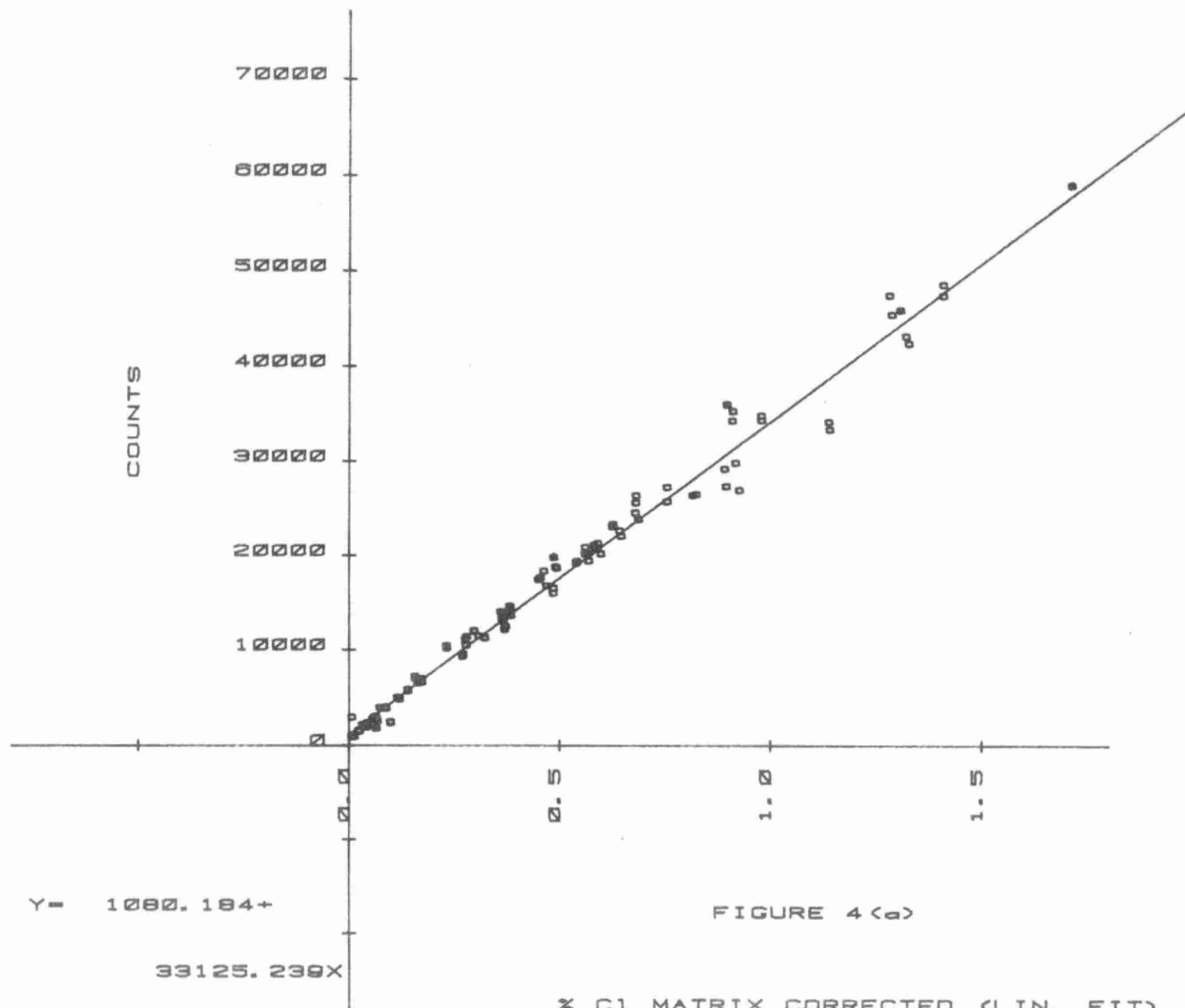


TABLE 3
SULPHUR AOAC VS XRF

%S					%S					%S				
Sample	Type	AOAC	XRF	Diff	Sample	Type	AOAC	XRF	Diff	Sample	Type	AOAC	XRF	Diff
2618W	coniferous	0.301	0.304	-1	402NW	grape	0.419	0.470	-12	256NW	coniferous	0.181	0.173	4
826W	coniferous	0.331	0.250	24	655NW	alfalfa	0.507	0.489	3	180NW	deciduous	0.189	0.202	7
1240W	coniferous	0.128	0.125	2	673W	alfalfa	0.485	0.543	-12	4306W	deciduous	1.118	1.137	2
2540W	coniferous	0.302	0.309	-2	3817W	ragweed	0.760	0.712	6	652W	alfalfa	0.274	0.303	-10
338W	coniferous	0.182	0.188	-3	2677W	fern	0.203	0.204	-1	2219W	tomato	3.630	2.910	19
92W	coniferous	0.103	0.107	-4	4351W	lily	0.134	0.121	10	2851W	barley	0.325	0.283	12
94NW	coniferous	0.163	0.128	21	754NW	hollyhock	1.648	1.716	-4	1213W	oats	0.845	0.806	5
2584W	coniferous	0.222	0.199	10	1218NW	garden produce	2.835	2.488	12	5191NW	grass	0.211	0.265	-25
2688W	deciduous	0.293	0.276	6	3507NW	garden produce	1.215	1.189	2	NBS	orchard leaves cert. value	0.190	0.191	-1
2658W	deciduous	0.475	0.445	6	1463W	garden produce	0.391	0.342	12	NBS	tomato leaves	-	0.644	
4340W	deciduous	0.390	0.394	-1	1191W	garden produce	0.250	0.265	-6	NBS	pine needles	-	0.118	
2467W	deciduous	0.158	0.166	-5	176W	garden produce	0.321	0.397	-23	NBS	spinach leaves	-	0.499	
2426W	deciduous	0.672	0.664	1	176NW	garden produce	0.452	0.491	-9	NBS	wheat flour	-	0.159	
2495W	deciduous	0.473	0.480	-2	1128W	corn	0.129	0.198	-53					
443NW	coniferous	0.159	0.159	0	30NW	corn	0.278	0.210	24					
161NW	coniferous	0.330	0.331	-1	170NW	barley	0.420	0.406	3					
906NW	coniferous	0.689	0.647	6	813W	oats	0.313	0.337	-8					
980W	shrubs	0.760	0.735	3	2419NW	forage	0.231	0.268	-16					
1211W	shrubs	0.384	0.395	-3	829W	coniferous	0.137	0.123	10					

$\sigma = 0.006$
precision : 0.017%
det. limit: 0.02%
accuracy:
(0-0.5%): $\pm 0.025\%$
(0.5-1.0%): $\pm 0.035\%$
(1.0-2.0%): $\pm 0.040\%$
(2.0-4.0%): $\pm 0.50\%$



R = 0.993

% C1 MATRIX CORRECTED (LIN. FIT)
 Solid Squares=Spiked NBS ORL.
 Not Included in Fit

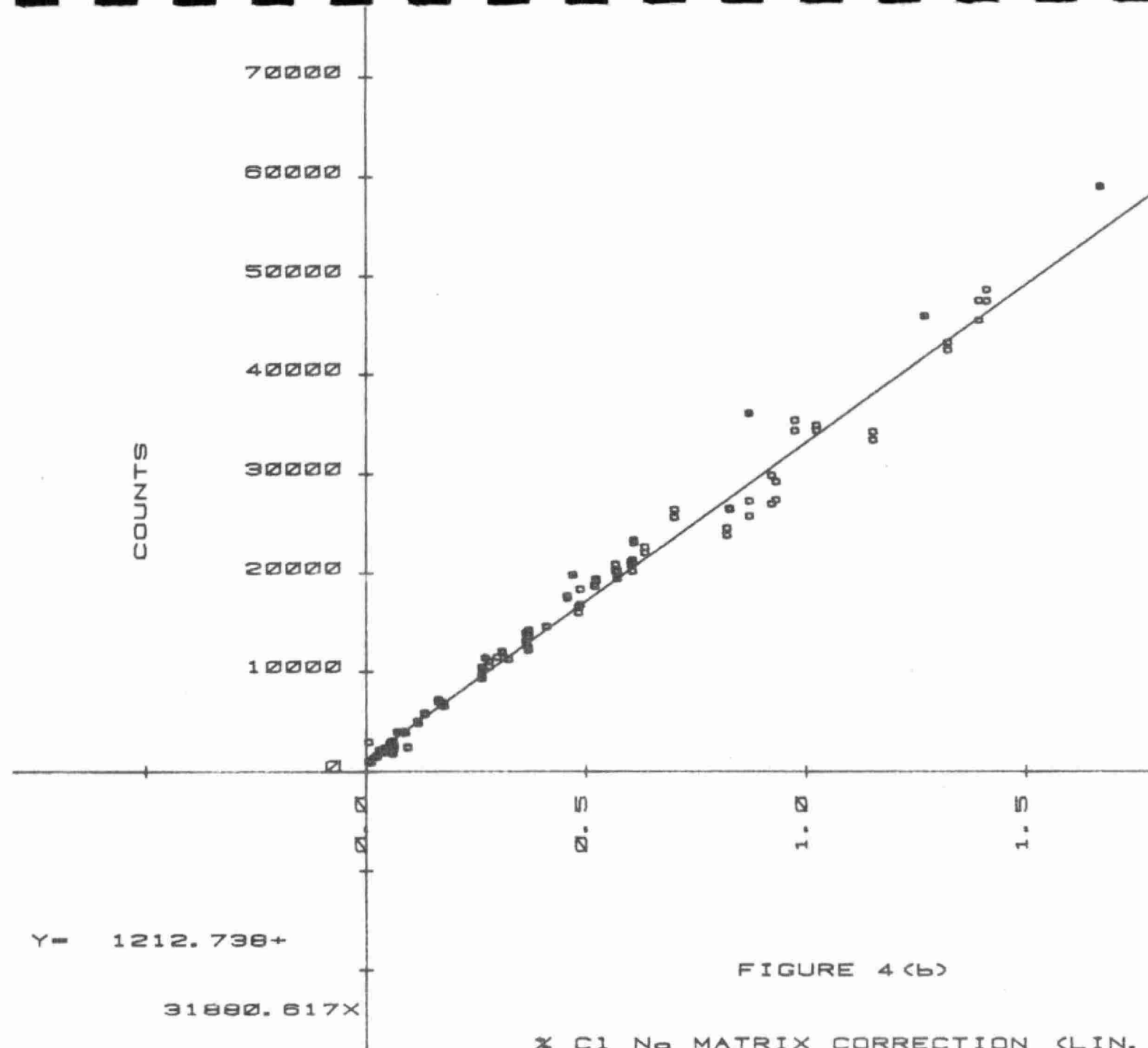


FIGURE 4(b)

X C1 No MATRIX CORRECTION (LIN. FIT)
 Solid Squares=Spiked NBS ORL. Not Included
 in Fit.

R= 0.994

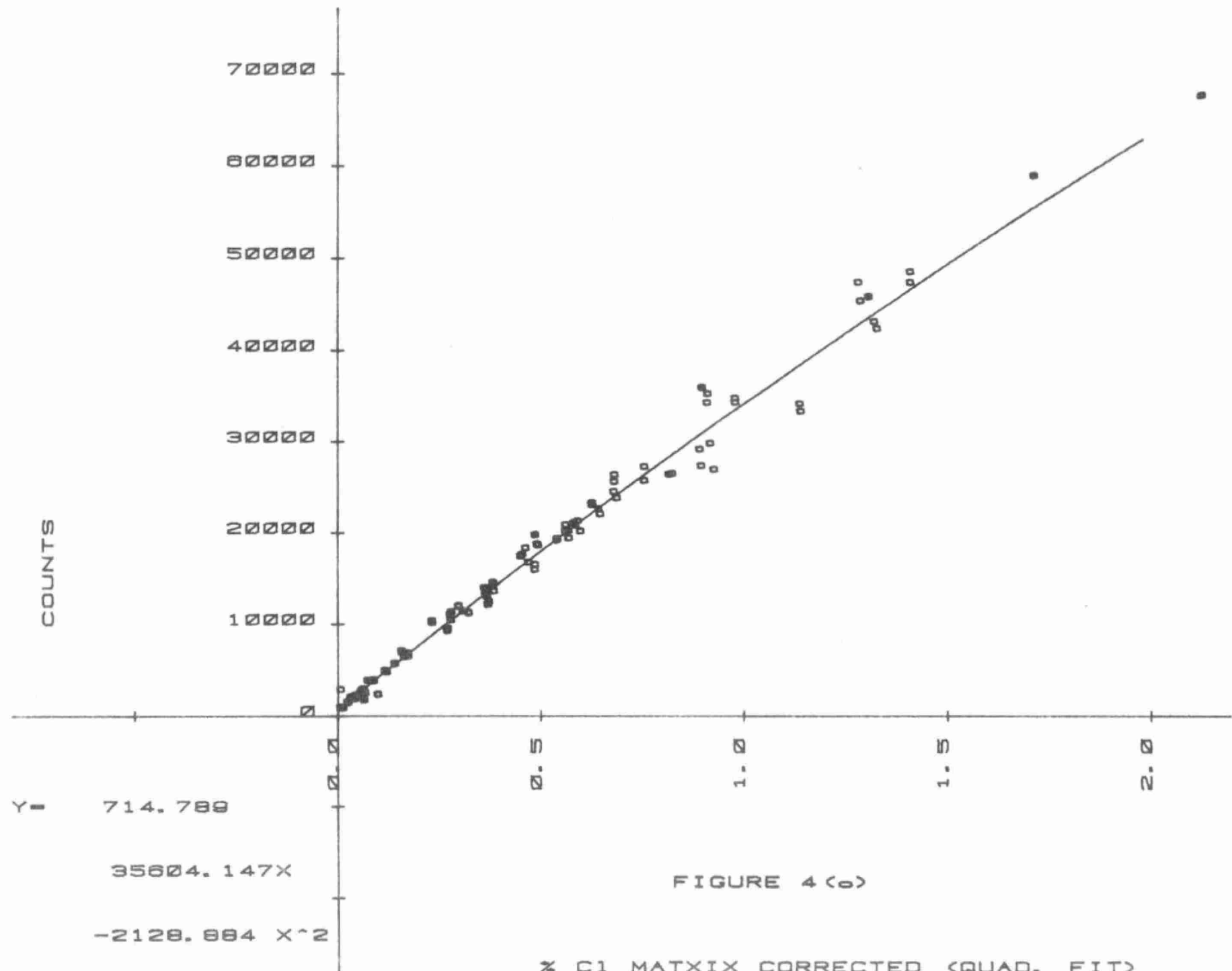


FIGURE 4 (c)

% C1 MATXIX CORRECTED (QUAD. FIT)

Solid Squares=Spiked NBS ORL.

Not Included in Fit

R 0.993

TABLE 4
CHLORINE AOAC VS XRF
QUADRATIC CALIBRATION CURVE

%Cl					%Cl					%Cl				
Sample	Type	AOAC	XRF	Diff	Sample	Type	AOAC	XRF	Diff	Sample	Type	AOAC	XRF	Diff
5813NW	coniferous	0.057	0.058	-2	1935NW	dogwood	0.164	0.189	-15	1719W	soy	0.279	0.291	-4
2359NW	coniferous	0.063	0.048	24	2080NW	dogwood	0.036	0.034	6	1701W	soy	0.118	0.116	2
1240W	coniferous	0.060	0.030	50	1242W	fern	0.520	0.554	-7	1637W	soy	0.040	0.033	18
350W	coniferous	0.133	0.135	-2	1242W	fern	0.309	0.337	-9	2689W	soy	0.603	0.611	-1
3068W	coniferous	0.056	0.046	18	1870NW	tansy	0.263	0.243	8	807W	corn	0.487	0.511	-5
3106W	coniferous	0.054	0.052	4	1891NW	tansy	0.826	0.765	7	1573W	corn	0.410	0.429	-5
3119W	coniferous	0.030	0.036	-20	1892NW	tansy	1.323	1.280	3	1147NW	corn	0.606	0.596	2
7251NW	deciduous	0.006	<.010	-	1901NW	tansy	0.634	0.623	2	1647W	corn	0.571	0.560	2
7253NW	deciduous	0.011	<.010	-	1925NW	tansy	0.369	0.333	10	1682W	corn	0.062	0.054	13
2467W	deciduous	0.089	0.093	-4	4181W	ragweed	1.362	1.009	26	1707NW	corn	0.567	0.584	-3
2539NW	deciduous	0.298	0.280	6	4117W	ragweed	0.932	0.850	9	1707W	corn	0.483	0.449	7
2637NW	deciduous	0.061	0.059	3	4211W	ragweed	0.367	0.376	-2	3071NW	grass	0.609	0.641	-5
2603NW	deciduous	0.523	0.523	0	4197NW	ragweed	1.024	1.062	-4	3071W	grass	0.370	0.369	0
2068NW	deciduous	0.364	0.365	0	673W	alfalfa	0.105	-	-	3104W	grass	0.177	0.181	-2
2495W	deciduous	0.117	0.123	-5	754NW	hollyhock	0.263	0.312	-19	2071NW	grass	0.922	0.820	11
906NW	deciduous	0.049	0.072	-47	902NW	grape	0.695	0.666	4	4206W		1.153	1.095	5
1704NW	dogwood	0.324	0.303	6	2219W	tomato	0.820	0.827	-2	4212W		0.458	0.496	-8
1211W	dogwood	0.171	0.170	2	838NW	tomato	0.821	0.877	-7	2592NW		0.701	0.776	-11
1526W	dogwood	0.024	0.022	8	3535NW	rhubarb	1.412	1.458	-3	3324NW	oats	1.394	1.524	-9
4198W	grass	0.975	1.098	-13										
NBS	Orchard Leaves	0.069	0.084	-21										
	cert. value													
NBS	tomato leaves		1.180	-										
NBS	pine needles		0.029	-										
NBS	spinach leaves		.887	-										
NBS	wheat flour		0.062	-										

$\sigma = 0.005$

precision : 0.014%

det. limit: 0.015%

accuracy :

(0-0.5%): ± 0.016

(0.5-1%): ± 0.030

(1.0-3.0%): ± 0.100

TABLE 5(a)
DILUTION OF NBS ORCHARD LEAVES

Sample	Dilution Factor	% Cl			%Cl		
		Theory*	Linear	Ave.	Theory*	Quad.	Ave.
1	1		0.077			0.082	
2	1	0.078	0.079	0.078	0.084	0.084	0.084
3	1		0.070			0.084	
4	$\frac{1}{2}$		0.037			0.044	
5	$\frac{1}{2}$	0.039	0.027	0.033	0.042	0.035	0.040
6	$\frac{1}{2}$		0.034			0.042	
7	$\frac{1}{4}$		0.012			0.021	
8	$\frac{1}{4}$	0.020	<0.010	0.010	0.021	0.019	0.019
9	$\frac{1}{4}$		<0.010			0.018	

*The theoretical value is equal to the undiluted value x the dilution factor.

TABLE 5 (b)
DILUTION OF NBS SPINACH LEAVES

Sample	Dilution Factor	%Cl			%Cl		
		Theory*	Linear	Ave.	Theory*	Quad.	Ave.
1	1	0.845	0.841	0.845	0.838	0.834	0.838
2	1		0.848			0.841	
3	3/4	0.634	0.675	0.675	0.628	0.665	0.665
4	3/4		0.674			0.664	
5	1/2	0.423	0.469	0.466	0.419	0.459	0.456
6	1/2		0.463			0.453	
7	1.5/4	0.317	0.348	0.353	0.318	0.350	0.346
8	1.5/4		0.358			0.341	
9	1/4	0.211	0.245	0.244	0.210	0.239	0.240
10	1/4		0.243			0.241	

* The theoretical value is equal to the undiluted value x the dilution factor.

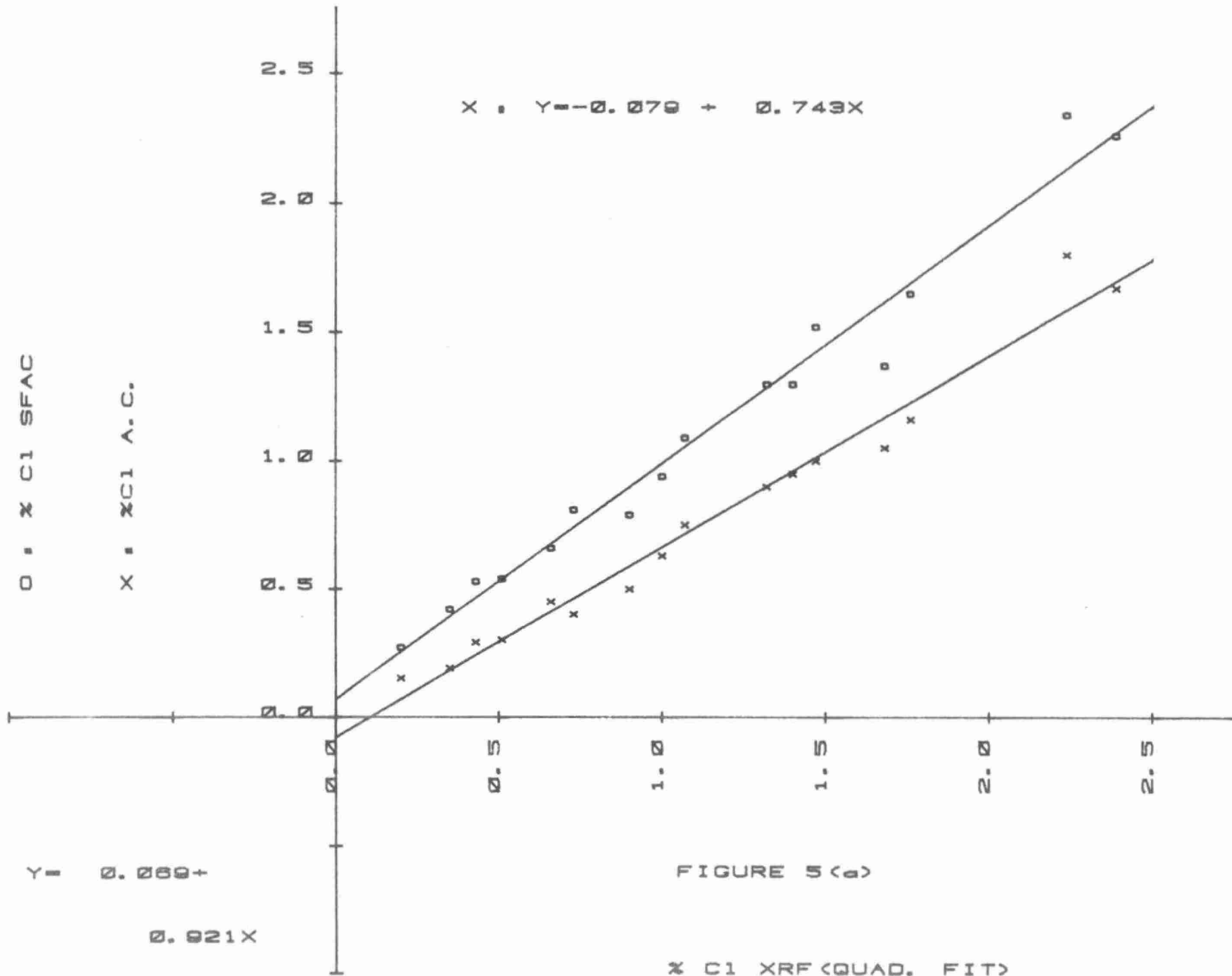


FIGURE 5(a)

% C1 XRF (QUAD. FIT)

R = 0.987

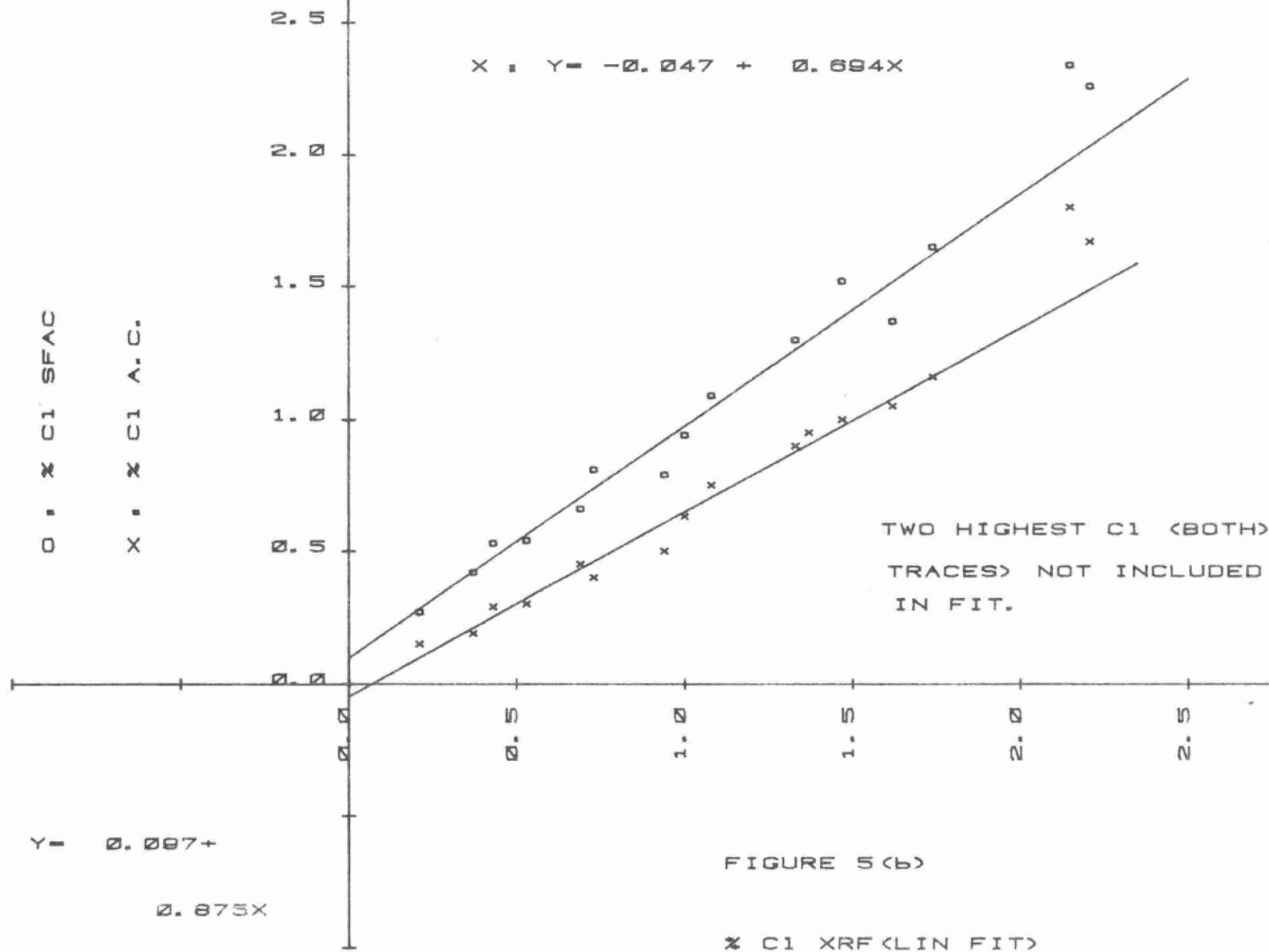


FIGURE 5(b)

R = 0.984

TABLE 5(c)
INTERLAB COMPARISON
Cl IN VEGETATION

SAMPLE	%Cl			
	A.C.	S.F.A.C.	LIN. XRF	QUAD. XRF
8260NW	0.30	0.54	0.53	0.51
8264NW	0.63	0.94	1.00	1.00
8264W	0.75	1.09	1.08	1.07
8267W	0.29	0.53	0.43	0.43
8271NW	1.05	1.37	1.62	1.68
8271W	0.95	1.30	1.37	1.40
8273W	0.19	0.42	0.37	0.35
8275NW	1.16	1.65	1.74	1.76
8275W	0.90	1.30	1.33	1.32
8277W	1.00	1.52	1.47	1.47
8278W	0.15	0.27	0.21	0.20
8281NW	0.50	0.79	0.94	0.90
8287W	0.45	0.66	0.69	0.66
8291NW	0.40	0.81	0.73	0.73
8293NW	1.67	2.26	2.21	2.39
8293W	1.80	2.34	2.15	2.24

S.F.A.C.: Combustion of the vegetation sample in a Schöniger Flask followed by analysis by a Technicon - Autoanalyzer.

A.C.: Combustion of the vegetation sample in a muffle furnace (temperature optimized for F^- recovery) and analysis by Technicon - Autoanalyzer.

XRF: Analyses performed by X-Ray Fluorescence Spectroscopy. Calibration curve obtained from A.O.A.C. analysed vegetation samples.

LIN.: Linear Fit to the A.O.A.C. data.

QUAD.: Quadratic Fit to the A.O.A.C. data

TABLE 5 (d)
RECOVERY DATA

Sample	% Cl	Added	Recovery (Linear)		Recovery (Quadratic)	
	(Total)	Cl (mg)	mg Cl	%	mg Cl	%
1	0.286	4.0	4.4	110	4.2	105
2	0.486	8.0	9.3	116	9.0	113
3	0.886	16.0	18.9	118	18.8	117
4	1.286	24.0	24.7	103	25.2	105
5	1.686	32.0	32.5	102	34.1	107
6	2.086	40.0	37.6	94	40.4	101

POTASSIUM AAS VS XRF

[illegible]

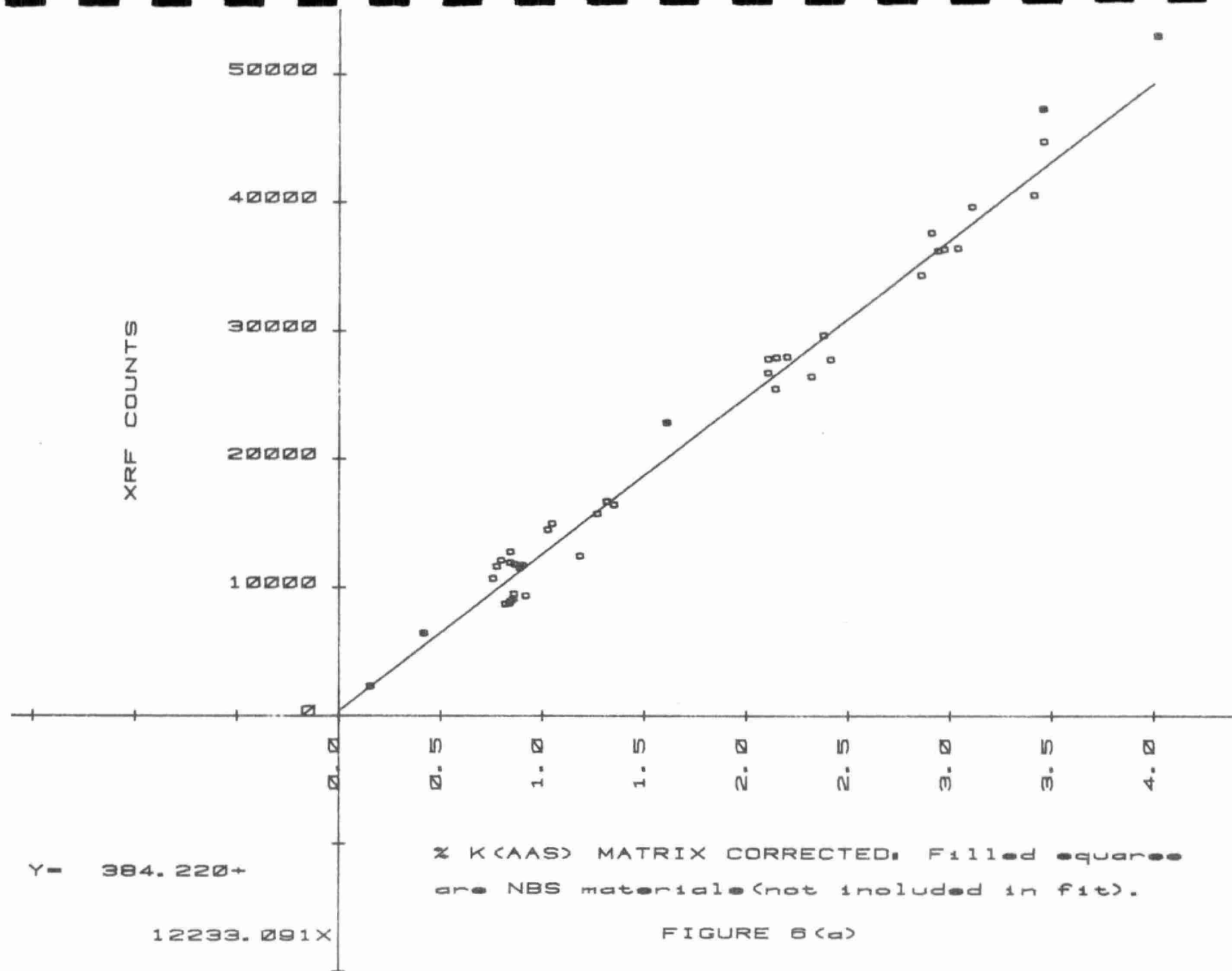
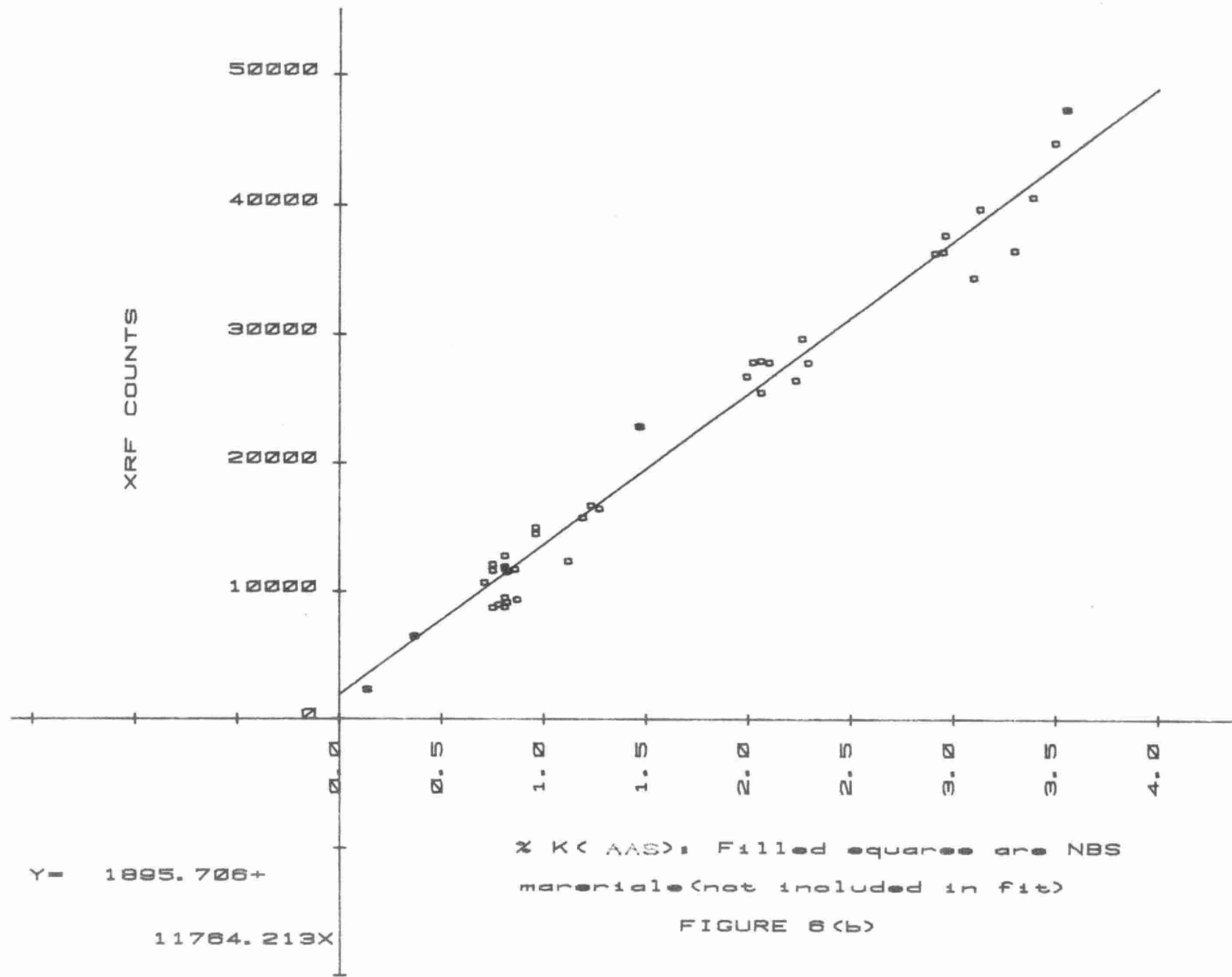


FIGURE 6(a)



$$Y = 1895.706 +$$

$$11764.213X$$

% K (AAS): Filled squares are NBS materials (not included in fit)

FIGURE 6(b)

$$R = 0.988$$

TABLE 6 (b)

RECOVERY DATA FOR K
ADDITION OF KCl TO NBS ORCHARD LEAVES

SAMPLE	%K	ADDED K (mg)	RECOVERIES K (mg)	% RECOVERY
1	1.78	4.4	5.5	125
2	1.93	8.8	8.82	100
3	2.46	17.6	19.4	110
4	2.84	26.4	27.1	103
5	3.21	35.2	34.4	98
6	3.48	44.0	40.0	91

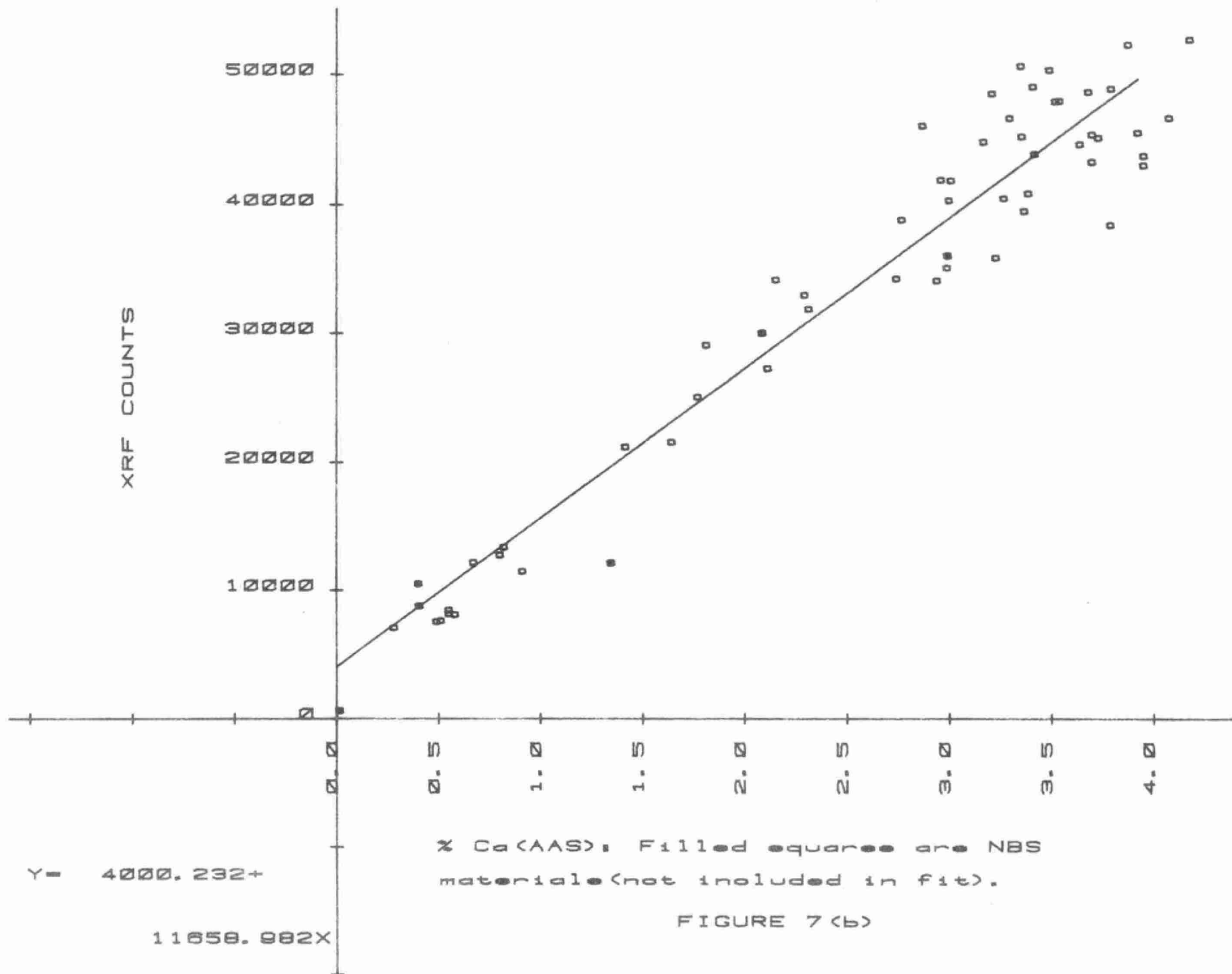
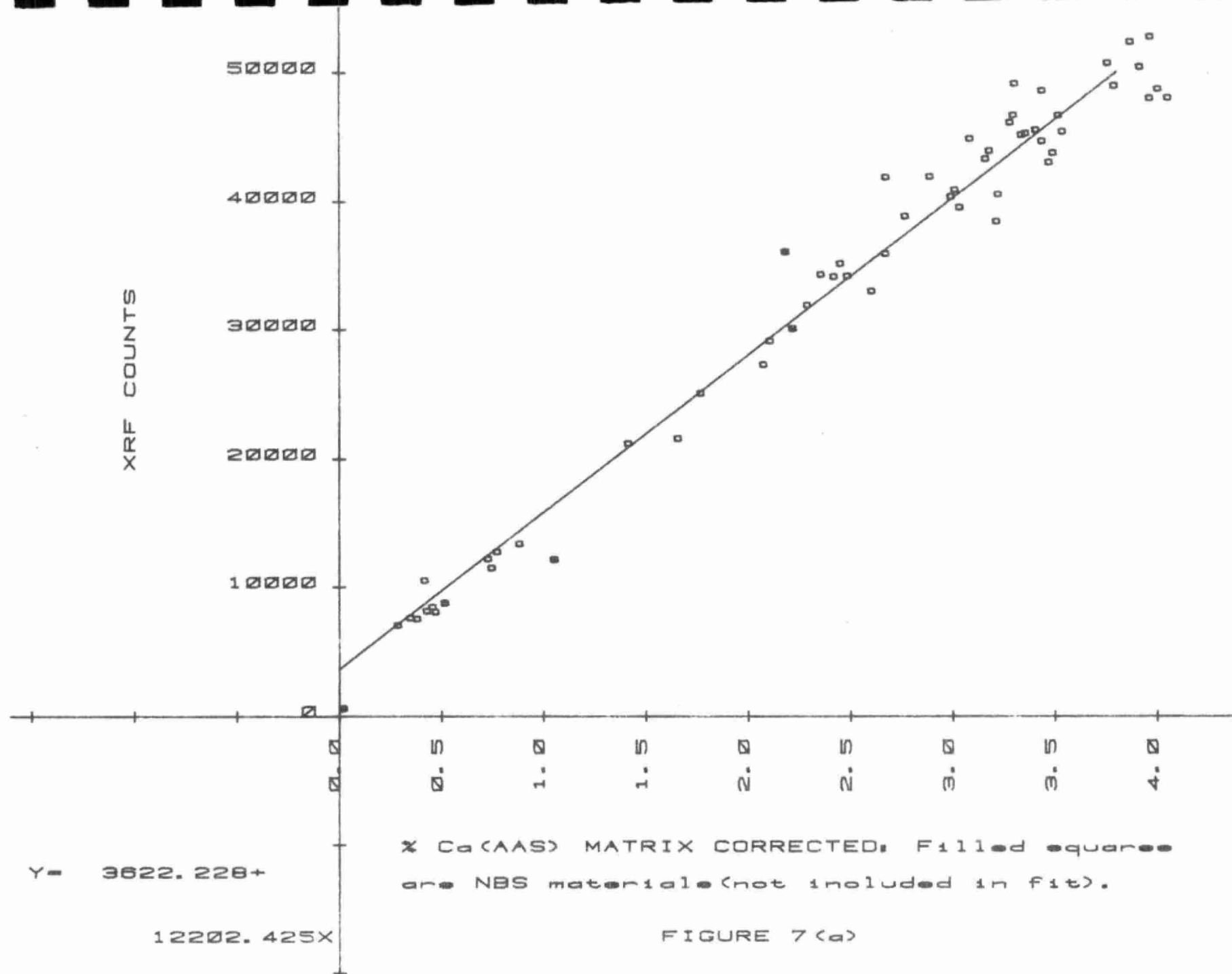


FIGURE 7 (b)

R = 0.965



% Ca (AAS) MATRIX CORRECTED: Filled squares are NBS materials (not included in fit).

TABLE 7
CALCIUM AAS VS XRF

Sample	Type	%Ca AAS	%Ca XRF	% Diff	Sample	Type	%Ca AAS	%Ca XRF	% Diff	Sample	Type	%Ca AAS	%Ca XRF	% Diff
3176W	Grass	0.28	0.27	3	3088W	Manitoba maple	3.35	3.45	-3	9289W	silver maple	1.25	1.29	-3
3097W	Grass	0.49	0.42	14	3085NW	Manitoba maple	3.68	3.44	6	9291NW	Manitoba maple	2.53	2.68	-6
3097NW	Grass	0.51	0.49	4	3084NW	Manitoba maple	3.21	3.50	-9	8901NW	silver maple	1.59	1.60	-1
3182W	Grass	0.55	0.49	10	3051NW	Manitoba maple	3.23	3.24	-1	9276NW	Manitoba maple	2.97	3.16	-6
3177W	Grass	0.80	0.79	1	3054W	Manitoba maple	3.70	3.63	2	9276W	Manitoba maple	2.74	2.98	-8
3177NW	Grass	0.91	0.80	12	3053W	Manitoba maple	3.95	3.76	5	9277NW	Manitoba maple	3.79	3.42	10
3231NW	Grass	0.55	0.49	10	3056NW	Manitoba maple	3.64	3.61	1	9277W	Manitoba maple	3.70	3.88	-5
3227W	silver maple	0.67	0.66	1	3055W	Manitoba maple	3.41	3.23	5	9278NW	Manitoba maple	3.39	3.51	-3
3228W	silver maple	0.82	0.76	7	3052W	Manitoba maple	3.95	3.72	5	9278W	Manitoba maple	3.01	3.61	-20
3226W	silver maple	0.40	0.56	-40	3056W	Manitoba maple	3.42	3.61	-5	9292NW	Manitoba maple	2.11	2.01	5
3185W	silver maple	1.81	1.80	1	3053NW	Manitoba maple	3.92	4.08	-3	9292W	Manitoba maple	2.31	2.38	-3
3160NW	silver maple	2.29	2.15	6	3054NW	Manitoba maple	4.17	4.29	-3	9303NW	Manitoba maple	3.27	3.12	-10
3160W	silver maple	2.15	2.20	-2	3052NW	Manitoba maple	4.07	4.01	1	9303W	Manitoba maple	3.00	3.08	-11
3095NW	Manitoba maple	3.73	3.86	-3	3055NW	Manitoba maple	4.04	3.92	3	9304NW	Manitoba maple	3.17	3.49	9
3093NW	Manitoba maple	3.37	3.32	1	9301NW	Manitoba maple	1.59	1.60	-1	9305NW	Manitoba maple	2.96	3.29	-5
3089W	Manitoba maple	3.52	3.27	7	9304W	Manitoba maple	3.39	3.61	-6	14124NW	grass	1.64	1.48	20
3089NW	Manitoba maple	3.49	3.47	1	9305W	Manitoba maple	3.45	3.56	-3	14126NW	cabbage	2.94	3.10	
3087W	Manitoba maple	3.54	3.22	9	9295NW	Manitoba maple	3.45	3.43	1	14127NW	cabbage	0.58	.46	
3087NW	Manitoba maple	2.87	3.10	-8	9295W	Manitoba maple	3.55	3.72	-5					

$\sigma = 0.028$
 $\sigma = 0.028$
precision: 0.078%
det. limit: 0.02%
accuracy: (0-1.0%): $\pm 0.06\%$
(1.0-2.5%): $\pm 0.10\%$
(2.5-4.5%): $\pm 0.19\%$

NBS orchard leaves 2.09 2.08 1
NBS tomato leaves 3.00 3.40 -13
NBS pine needles 0.41 0.34 17
NBS spinach leaves 1.35 0.91 32
NBS wheat flour 0.19 0.20 -

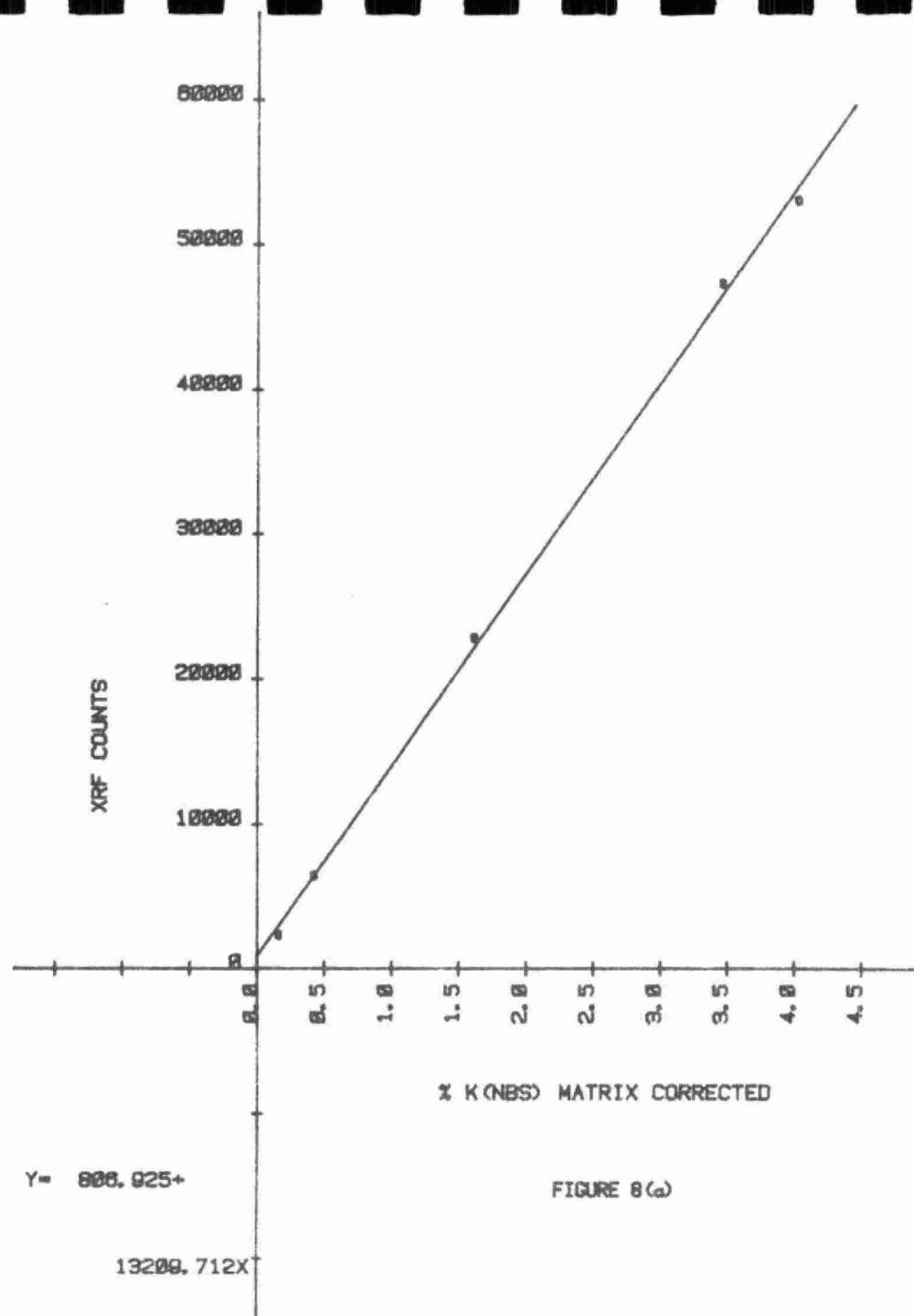


FIGURE 8(a)

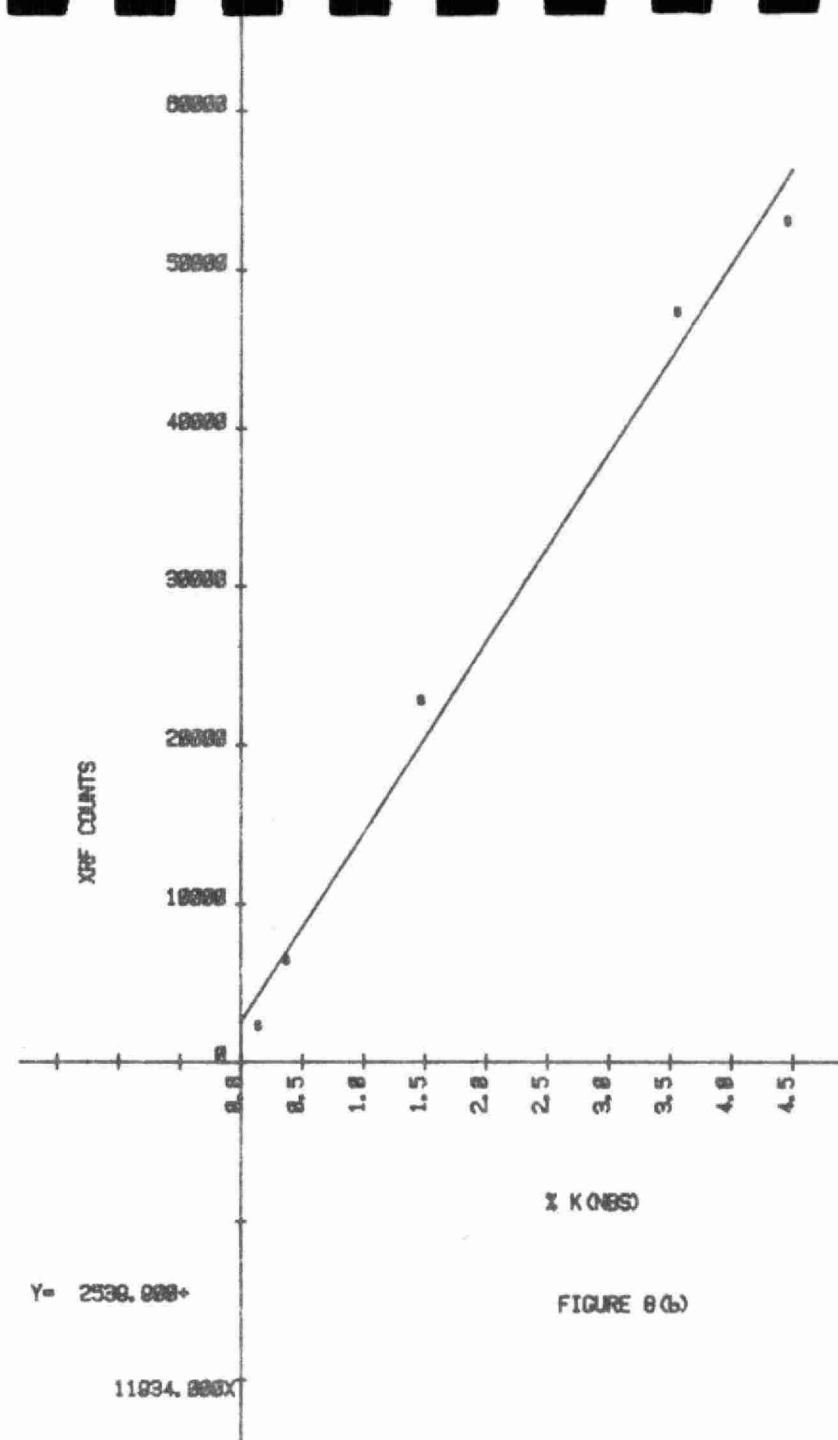
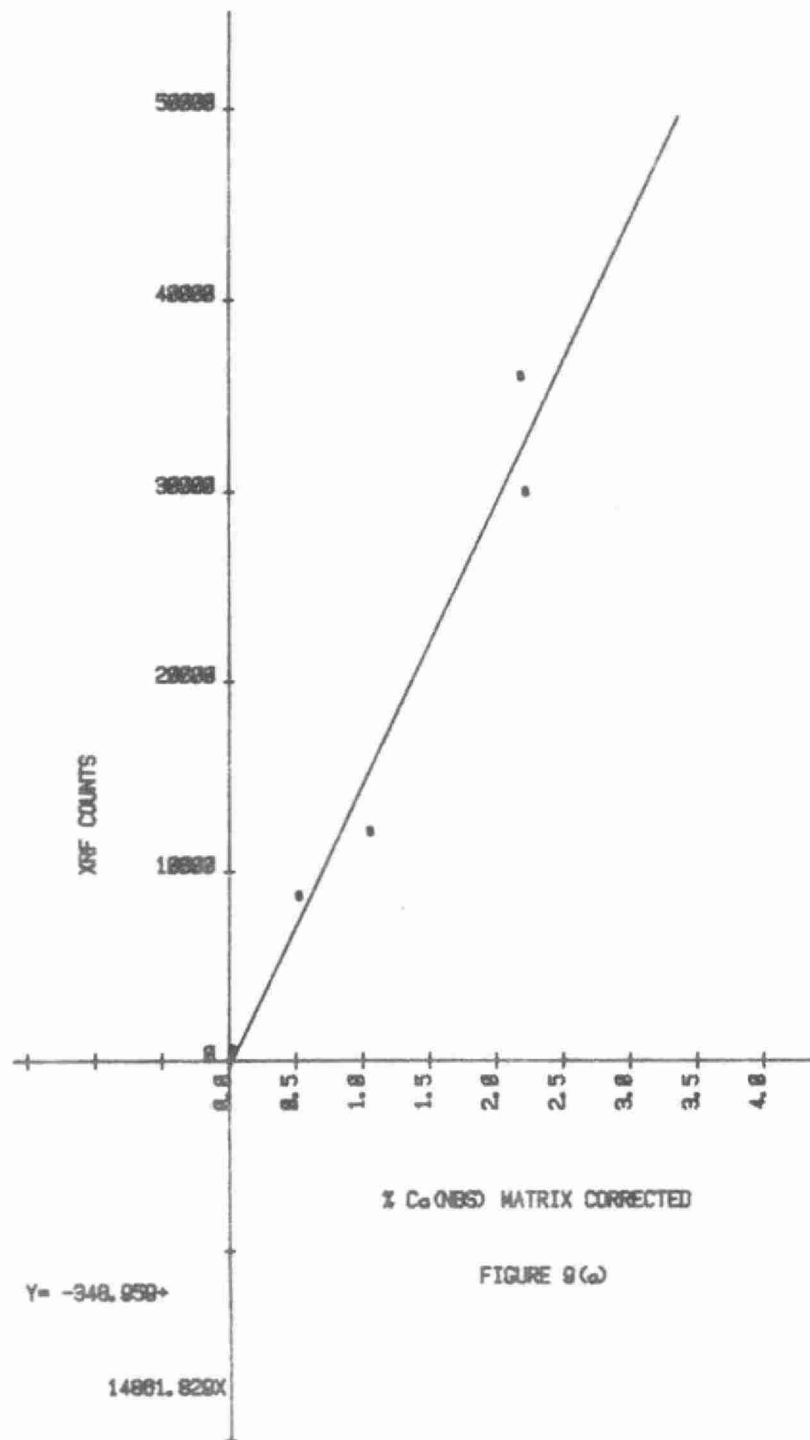
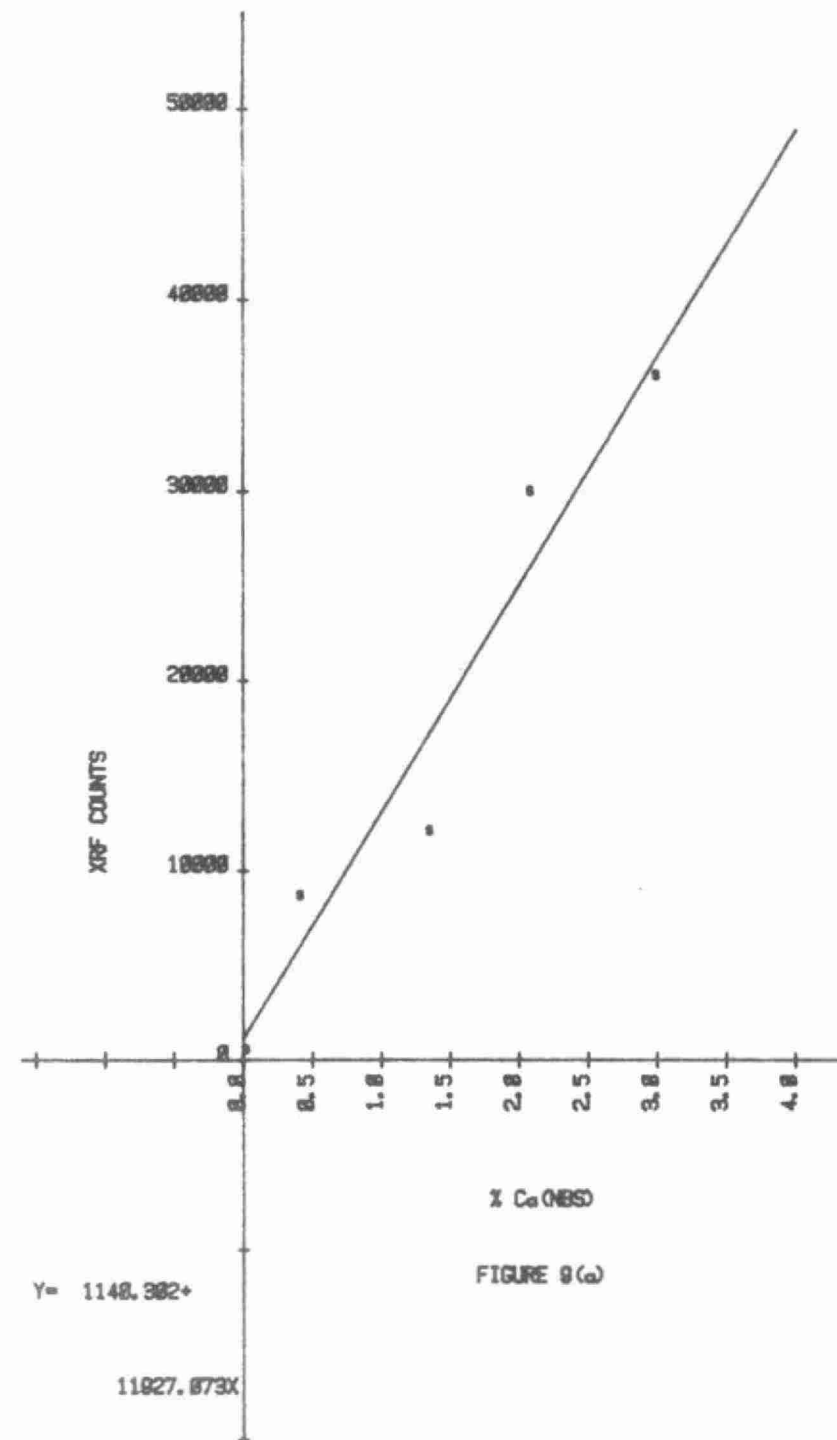


FIGURE 8(b)



R= 0.988



R= 0.971

MOE/ANA/AMWN

Judge, R H

The analysis of

vegetation by x-ray amwn

c.2 a aa

MOE/ANA/AMWN



(9115)